AGRICULTURAL RESEARCH INSTITUTE

PUSA

PROCEEDINGS

OF THE

ROYAL SOCIETY OF LONDON

SERIES A

CONTAINING PAPERS OF A MATHEMATICAL AND
PHYSICAL CHARACTER.

VOL. CI.

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SERIES A. VOL. CI.

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β-Ray Spectra and their Meaning.

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Introduction.

In a previous paper,[*] I described some measurements of the magnetic spectrum of the β-rays ejected from various metals by the γ-rays of radium B. These experiments showed that the conversion of monochromatic γ-rays into β-rays was described by the same quantum relation that holds for X-rays and light, and using this knowledge it was found possible to give a complete explanation of the natural β-ray spectrum of radium B. Sir Ernest Rutherford[†] had already shown that the lines in the β-ray spectrum were due in some way to the conversion of monochromatic γ-rays in the same radio-active atom that emitted them, and these experiments on the excited spectra now proved that the strong lines were due to the conversion of the γ-rays in the K ring, and the weaker lines to conversion in the L_3 ring.

This explanation of the line β-ray spectrum is, by itself, of considerable interest, but of far greater importance is the fact that these experiments give a method of finding the wave-lengths of γ-rays. The shortest wave-length that has been measured by the crystal method is 0·07 Å.U.,[‡] and at present it seems almost impossible to extend this range much further by this method. Since many radio-active bodies emit γ-rays of shorter wave-length than this any method by which these wave-lengths may be found is important.

The method is as follows : The first step is to measure the energies of the different lines in the natural β-ray spectrum of the body. If a certain line

[*] Ellis, 'Roy. Soc. Proc.,' A, vol. 99, p. 261 (1921).

[†] Rutherford, Robinson and Rawlinson, 'Phil. Mag.,' vol. 28, p. 281 (1914) ; Rutherford 'Phil. Mag.,' vol. 34, p. 153 (1917).

[‡] Rutherford and Andrade, 'Phil. Mag.,' vol. 28, p. 263 (1914).

corresponds to an energy E_1, and is produced by the conversion of a γ-ray of frequency ν

$$E_1 = h\nu - w_1,*$$

where w_1 represents the work to remove the electron from its position inside the atom to the surface. To find the frequency of the γ-ray all that is necessary is to determine the quantity w_1. This may be done by measuring the energy of the corresponding line in the excited spectra of a body of neighbouring atomic number. In this second case the electron will come from the corresponding level, but the work done in removing it to the surface of the atom will be different w_2. The difference in the energies of the two corresponding β-ray lines $E_2 - E_1$ is clearly equal to $w_1 - w_2$, and is determined directly. To find w_1, all that is necessary is to see which of the corresponding levels of the two atoms differ by this amount. This can be done from the X-ray absorption data, which also gives the absolute magnitude of w_1.

Where this method can be applied it leads to perfectly definite results, but it is not always possible to obtain sufficiently strong sources to enable excited spectra to be measured. In this case the natural β-ray spectrum has to be analysed by inspection. Very frequently two or more lines can be found which differ in energy by the same amount as certain known levels in the atom, for instance, the K and the L levels, or the $L_3L_2L_1$ levels. It is then reasonably certain that the β-ray lines in question originate in these levels by the action of the same γ-ray.

The γ-rays of radium B, radium C, and thorium D have been investigated by these methods, and the measurements are given in the following sections. There is considerable evidence that these γ-rays come from the nucleus and are characteristic of its structure, and it is already possible from these measurements to obtain some information about this structure. This is of special interest since, at the moment, there seems to be no other method of attacking the problem of the structure of the heavy nuclei.

The γ-Rays of Radium B.

The complete β-ray spectrum of radium B, as measured by Rutherford and Robinson,† is shown in the next Table.

The first eleven lines were analysed by the excited spectrum method, and the results were given in the paper already referred to.‡ These lines

* The experiments described on pp. 264 and 265 of the previous paper have been extended to include Ag (At. No. 47). The values of the γ-ray energies deduced are 2·93 and 3·48 × 10⁵ volts. This gives a sufficient range of atomic number to show that the equation $E = h\nu - w$ is exact.

† Rutherford and Robinson, 'Phil. Mag.,' vol. 26, p. 717 (1913).

‡ Ellis, *loc. cit.*

are due to six γ-rays of wave-length of the order of 0·04 Å.U., ejecting electrons from the K and L_3 levels of the radium B atom. The diffuse groups 12 and 13 have now also been analysed by the same method, using the same experimental arrangement.

Table I.—Groups of β-Rays from RaB.

(Measured by Rutherford and Robinson.)

No.	Energy of group in volts.	No.	Energy of group in volts.
1	$3·851 \times 10^5$	9	$2·031 \times 10^5$
2	3·473	10	1·645
3	3·328	11	1·494
4	3·103	12	0·743–0·694
5	2·756	13	0·618–0·585
6	2·608	14	0·535
7	2·864	15	0·500
8	2·227	16	0·375

Two corresponding groups of slightly greater energy were observed in the excited β-ray spectrum of platinum, and the increase of energy agreed with the difference in energy between the L levels of lead and platinum, showing that these groups are due to the conversion of γ-rays in the L ring. The γ-rays in question are the "K" X-radiations of radium B, the first group being due to $K_β$ and $K_γ$, and the second group to $K_α$. This may be seen from Table II.

The agreement is fair, but not very good, and another point is that this Table indicates a series of lines and not the diffuse groups actually observed. The same causes probably explain both facts. Radium C emits β-rays in this region,* which almost certainly have the same origin, but the energies will be slightly greater. Again, it must be remembered that the groups are due to the ejection of an electron from the L ring of an atom by the radiation emitted by an electron returning to the K ring of the same atom, and returning either from or through this L ring. Under these circumstances it is unlikely that calculations based on the normal L levels can be very accurate.

The origin of the remaining prominent β-ray lines numbered 14, 15, and 16 has not been determined. Several attempts were made to measure the corresponding lines in lead and platinum, but no satisfactory results were obtained. The experimental method is not suitable for these low velocities, and it was not anticipated that excited lines corresponding to the less prominent lines 14 and 15 would be obtained, but No. 16 is a very strong one and should have yielded results. This line in the natural spectrum

* Rutherford and Robinson, *loc. cit.*, p. 727.

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Table II.—Showing Origin of β-Ray Groups 12 and 13 of Table I.

RaB K lines.		RaB L levels.‡	
λ in Å.U.	Energy in volts.	λ in Å.U.	Energy in volts.
Kα ... 0·169	0 731 × 10⁶ *	L₁ ... 0·9487	0·180 × 10⁶
Kβ ... 0·149	0·829†	L₂ ... 0·8128	0·152
Kγ ... 0·143	0·864†	L₃ ... 0·7808	0·158

Origin of group.	Energy of group in volts. (Calculated.)	Energy of group. (Observed.)
Kα—L₃	0·578 × 10⁵	⎫ 0·585 × 10⁵
Kα—L₂	0·579	⎬ to
Kα—L₁	0·601	⎭ 0·618
Kβ—L₃	0·671	⎫
Kβ—L₂	0·677	⎪
Kβ—L₁	0·699	0·694
Kγ—L₃	0·706	to
Kγ—L₂	0·712	0·748
Kγ—L₁	0·734	⎭

* Ledoux-Lebard and Dauvillier, ' Physique des Rayons,' X, p. 75.
† Ledoux-Lebard, loc. cit. (extrapolated).
‡ Ledoux-Lebard, loc. cit., p. 69.

appears to be almost a narrow band, and it is possible that it is composed of β-rays of different origins. For instance, the γ-ray of wave-length 0·099 Å.U., measured by the crystal method by Rutherford and Andrade, would eject an electron of this energy from the K ring, and again, the γ-ray 0·229 Å.U. acting on the L₃ ring would fit the results, and the same γ-ray acting on the M and exterior rings might give lines 15 and 16. Some evidence on these possibilities has been obtained from excited spectra, but it would require a large amount of work to complete the analysis.* The general evidence indicates that the β-ray emission in this region is due to the γ-rays measured by Rutherford and Andrade by the crystal method, and since the wave-lengths had been determined accurately already, it was not thought necessary to carry the β-ray method any further.

The γ-ray spectrum of radium B extends without any appreciable gaps from 0·03 Å.U. to the L X-ray region, about 1·3 Å.U., and the wave-lengths of all the main lines are now known.

* Some recent experiments suggest strongly that this group is due to the γ-ray λ = 0·229 Å.U., as described in the text.

The γ-Rays of Radium C.

The β-ray spectrum of radium C has been measured by Rutherford and Robinson,* and their results are shown in the next Table. This only includes the lines up to energy 5.94×10^5 volts; the lines of greater energy will be treated in a subsequent paper.

Table III.—The β-Ray Groups of RaC.
(Measured by Rutherford and Robinson.)

No.	Intensity.	Energy in volts.
H	m.s.	5.94×10^5
36	m.f.	5.67
37	m.f.	5.44
K	s.	5.15
39	f.	4.91
40	f.	4.79
41	m.f.	4.48
42	f.	4.05
43	f.	3.33
L	m.	2.96
M	m.	2.59
N	m.	1.81
47	f.	1.59
48	f.	1.49

These β-rays have been investigated by the excited spectrum method.

The line corresponding to K in Table III was observed excited in platinum and uranium, and the results are shown in the next Table.

Table IV.

Metal.	Atomic number.	Energies in volts.
Platinum	78	5.28×10^5
Radium C...............	88	5.15
Uranium	92	4.86

It is seen that there is a large shift, which suggests the K ring as the origin of the line. This is proved by adding to each of the above values the corresponding K absorption energy, respectively

$$0.78 \qquad 0.92 \qquad 1.18 \times 10^5 \text{ volts,}$$

when the following values are obtained for the γ-rays energy,

$$6.06 \qquad 6.07 \qquad 6.04 \times 10^5 \text{ volts.}$$

The agreement is thus very good.

* Rutherford and Robinson, *loc. cit.*

The line H is certainly the result of this same γ-ray ejecting electrons from the L_3 ring. For in this case the energy would be

$$\gamma\text{-ray energy minus } L_3 \text{ absorption energy.}$$

For radium C this would give

$$(6{\cdot}07 - 0{\cdot}16) \times 10^5 = 5{\cdot}91 \times 10^5,$$

and Rutherford's measurement is $5{\cdot}94 \times 10^5$.

It was found possible to make approximate measurements of the corresponding line from uranium,

Calculated...... $(6{\cdot}07 - 0{\cdot}22) \times 10^5 = 5{\cdot}85 \times 10^5$,

Measured .... $5{\cdot}91 \times 10^5$.

There is, therefore, conclusive evidence that radium C emits a γ-ray of characteristic energy,

$6{\cdot}07 \times 10^5$ volts,   wave-length $0{\cdot}0203$ Å.U.

It is extremely probable that the remaining lines in the β-ray spectrum are the result of five or more weaker γ-rays ejecting electrons from the K and L_3 rings, but the γ-rays are not sufficiently intense for measurements of the excited spectra to be possible. A certain amount, however, can be deduced by inspection.   There are three pairs of lines 36 and 39, 40 and 42, and M and N showing a constant difference of energy equal to the difference of the K and L_3 absorption energies of radium C, that is $0{\cdot}76 \times 10^5$ volts. This indicates that these six lines are due to the conversion in the K and L_3 rings of three γ-rays, and the characteristic energies of these γ-rays are obtained by adding to the energies of the β-ray lines the K absorption energy $0{\cdot}92 \times 10^5$ volts and the L_3 absorption energy $0{\cdot}16 \times 10^5$ volts respectively.

The γ-rays of radium C which have been found are collected in the next Table. This list includes all the prominent γ-rays of wave-length greater than $0{\cdot}02$ Å.U. with the exception of the one giving the line L. It seems very likely that this line is due to the conversion in the K ring of a γ-ray of energy $3{\cdot}88 \times 10^5$ volts and wave-length $0{\cdot}0318$ Å.U., but since this is not certain it is not included in the Table.

Table V.—γ-Rays of RaC.   (Deduced from the β-Ray Spectrum.)

Intensity.	Energy in volts.	λ in Å.U.
m.	$2{\cdot}74 \times 10^5$	0·0450
f.	4·96	0·0249
f.	5·83	0·0212
s.	6·07	0·0203

The β-Rays of ThC and D.

The measurements of the β-ray spectrum were made by the original method of Rutherford and Robinson,* using as source a small nickel plate 3 mm. by 10 mm. with the active material deposited on it. This has several advantages over the usual thin wire. It is easier to prepare, it can easily be arranged that all the active material is on one side so that it is all effective, and lastly the area of such a source is relatively large and, with a given quantity of radioactive substance from which the active material is to be obtained, the amount deposited is approximately proportional to the area.

Table VI.—Groups of β-Rays from ThC + D. (Measured by Ellis.)

Number.	Intensity.	Energy in volts. (Observed.)	Origin.	γ-ray.	Energy in volts. (Calculated.)
1	f.	$8·02 \times 10^5$			
2 A	m.s.	7·74			
3	m.f.	6·96			
4 B	m.s.	6·37	L_2	1	6·39
5 C	m.s.	5·68	K	1	5·67
6	m.f.	5·35			
7	m.f.	5·09			
8 D	v.s.	4·97	L_2	2	4·96
9 E	v.s.	4·24	K	2	4·24
10	f.	3·88			
11	f.	3·47			
12 F	m.s.	2·71	L_2	3	2·71
13 G	m.s.	2·59	L_2	4	2·59
14	m.f.	2·44			
15	m.	2·395	L_2	5	2·39
16	f.	2·32	L_2	6	2·33
17	m.f.	2·12	L_2	7	2·13
18 H	s.	1·992	K	3	1·99
19	m.f.	1·908	L_2	3	1·91
20 K	v.s.	1·869	K	4	1·87
21	m.	1·665	K	5	1·67
22 L	m.s.	1·614	K	6	1·61
23	f.	1·505			
24 M	m.s.	1·421	K	7	1·41
25	f.	1·247			
26 N	m.s.	1·197	K	8	1·19
27	m.	1·040			
28	f.	0·880			
29	f.	0·748			
30	f.	0·563			
31	m.	0·412	L_2	9	0·413
32	s.	0·406	L_2	9	0·406
33	m.	0·387	M_1	10	0·384
34 O	v.s.	0·375	M_2	10	0·377
35	m.	0·280	L_1	10	0·281
36	s.	0·261	L_2	10	0·261
37 P	v.s.	0·254	L_2	10	0·254

A source of this size, if used in the ordinary way, would give very poor focussing, but this can be avoided by tipping it towards the

* Rutherford and Robinson, *loc. cit.*

photographic plate so that the effective β-rays come off at nearly grazing incidence.

Sources of thorium C and D were obtained by immersing the nickel plate in a hot acid solution of radiothorium for about half an hour. The average source was 2 to 3 mgrm. The purity was always verified by measuring the decay. Since both thorium C and thorium D emit β-particles and both were present on the active sources it is impossible to tell to which body the β-ray lines belong. This point is treated in detail later.

The β-ray emission has been investigated from $2 \cdot 0 \times 10^4$ volts to $1 \cdot 9 \times 10^6$ volts. Over the whole of this range there is a background of continuous β-ray emission with a maximum of photographic effect about $2 \cdot 0 \times 10^5$ volts. A great many β-ray lines have also been measured and the results are shown in the first three columns of the next Table. The last seven lines were given in the previous paper but are repeated here for completeness. There was an error in the calculation of line 33 which is now corrected. All these measurements refer to Rutherford and Robinson's[*] determination of the β-rays of radium B as standard.

Hahn[†] found a broad band in the region $8 \cdot 70$ to $11 \cdot 2 \times 10^5$ volts, but in the present experiments no lines were found above $8 \cdot 0 \times 10^5$ volts.

The γ-rays of ThD.

Sufficiently strong sources of thorium C and D cannot be obtained to make the measurement of excited spectra practicable, so the deduction of the γ-rays from the β-ray spectrum has to be done by inspection. From analogy with radium B and C it is to be expected that the β-rays in the region $1 \cdot 2$ to $6 \cdot 0 \times 10^5$ volts will be due to conversion of γ-rays in the K and the L_3 rings. If this is so it should be possible to group the lines in pairs, the energy difference between the members of a pair being equal to the K absorption energy minus the L_3 absorption energy, and the line due to conversion in the K ring should be the stronger one of the pair.

There is another difficulty, however, because it is not known whether these lines are to be ascribed to thorium C (atomic number 83) or to thorium D (atomic number 81). Many attempts were made to take β-ray photographs with a pure source of thorium D prepared by recoil, but no definite results were obtained. Large sources of active material would be necessary in order to settle this question, and the whole problem is made more difficult by the short period of thorium D ($3 \cdot 1$ minutes).

Measurements on the absorption of the γ-radiation emitted by thorium C

* Rutherford and Robinson, *loc. cit.*
† Hahn, 'Phys. Zeit.,' vol. 12, p. 273 (1911).

and thorium D, throw some light on this point. Thorium C emits γ-rays only in small quantities, and the main γ-radiation of thorium C + D is to be ascribed to thorium D*, which would suggest that these β-ray lines are certainly not due to thorium C and so presumably come from thorium D. Against this is to be noted that nearly all of the γ-radiation from thorium D is of one very hard type,† and no evidence was obtained of softer γ-rays or of the characteristic K and L radiations which would result from the ejection of electrons from the K and L rings. This may not be a very serious objection since at first similar results were found for radium C, and it was only later that Richardson‡ detected softer γ-rays and the K radiations.

The internal evidence from the β-ray lines suggests strongly that they come from thorium D (atomic number 81), since all of the strong lines can be coupled in pairs, having a difference of energy 0.72×10^5 volts equal to the difference in energy of the K and L absorptions of a body of atomic number 81. Compared to the eight pairs found in this way only two pairs can be found to agree with thorium C (atomic number 83) corresponding to a separation of 0.76×10^5 volts.

The agreement that is obtained if these lines be assigned to thorium D may be seen from the last three columns of Table VI. The fourth column shows the origin of the line, the fifth column shows which of the γ-rays given in Table VII produces the line, and the last column gives the calculated energies.

On these grounds it will be assumed provisionally that these lines are due to thorium D, and the same assumption will be made about the last seven lines, due to conversion in the L rings, although neither the absorption measurements nor the β-ray evidence throw any light on the origin of this group.

These seven lines may be due to three γ-rays of characteristic energies $0.408, 0.531, 0.540 \times 10^5$ volts, ejecting electrons from the L rings. This view was put forward in the previous paper. It is also possible that they are produced by only two γ-rays, the first one (No. 10) ejecting electrons from the M ring as well. The agreement obtained on this hypothesis can be seen from Tables VI and VII. Approximate values for the M absorption voltages were obtained by interpolation ($M_1 = 0.024 \times 10^5$, $M_2 = 0.031 \times 10^5$).§

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* Rutherford and Richardson, 'Phil. Mag.,' (2), p. 937 (1913) ; Meitner and Hahn, 'Phys. Zeit.,' vol. 14, p. 873 (1913).
† Rutherford and Richardson, *loc. cit.*
‡ Richardson, 'Roy. Soc. Proc.,' A, vol. 91, p. 396 (1915).
§ Coster, 'Zeit. f. Physik,' [5], p. 139 (1921).

It is not possible to settle definitely which of these explanations is correct, but the results obtained from some recent experiments support the view given in this paper.

The γ-rays of thorium D are shown in the next Table. The absorption voltages used are also given.

Table VII.—γ-Rays of ThD.   (Deduced from the β-Ray Spectrum.)

Number.	Energy in volts.	λ in Å.U.
1	$6 \cdot 54 \times 10^{5}$	0 ·0189
2	5 ·11	0 ·0241
3	2 ·86	0 ·0431
4	2 ·74	0 ·0450
5	2 ·54	0 ·0486
6	2 ·48	0 ·0498
7	2 ·28	0 ·0541
8	2 ·06	0 ·0599
9	0 ·560	0 ·220
10	0 ·408	0 ·302

Absorption Voltages ThD.   (At. No. 81.)

Ring.	Energy in volts.	λ in Å.U.
K	$0 \cdot 869 \times 10^{5}$	0 ·1427*
L_3	0 ·154	0 ·808†
L_2	0 ·147	0 ·840†
L_1	0 ·127	0 ·974†

* Siegbahn and Jönsson, ' Phys. Zeit.,' vol. 20, p. 252 (1919).
† Ledoux-Lebard and Dauvillier, ' Physique des Rayons X,' p. 69.

Discussion.

The monochromatic γ-rays emitted by several radioactive bodies have been investigated by the β-ray method, and it is of interest to compare these results with those obtained by absorption measurements. The absorption method can only effect a rough analysis of the total γ-ray emission into several types, each type being absorbed according to a simple exponential law. This analysis cannot be very detailed, and it would be impossible to differentiate between a single line and the number of lines grouped around one of greater intensity.

The γ-rays of radium B have been investigated most completely, and it is best to make the comparison between the two methods for this body.

The total γ-ray spectrum of radium B is shown in the next Table. The first column contains the γ-rays of radium B and C as measured by Rutherford

and Andrade,[*] by the crystal method ; the second column the γ-rays measured by the writer, by the β-ray method. All of those in the second column come from radium B, whereas those in the first column are an unresolved mixture, some coming from radium B and some from radium C. In addition, Rutherford and Andrade measured the complete L and K spectra which are excited by the γ-rays, these are summarised under the heads L and K groups. The μ/ρ of the different types of radiation detected by Rutherford and Richardson[†] are given in the following Table :—

Table VIII.—The γ-Rays of RaB and C.

RaB and C. (Measured by Crystal, Rutherford and Andrade.)	RaB. (Deduced from the β-Ray Spectrum, Ellis.)		
λ in A.U.	Intensity.	λ in Å.U.	Energy in volts.
L spect. RaB			
L spect. RaC	v.s.	0·0519	$2·365 \times 10^5$
1·365 ⎫	m.s.	0·0488	2·529
1·286 ⎪			
1·266 ⎪	v.s.	0·0423	2·918
1·219 ⎬—" a "			
1·074 ⎪	v.s.	0·0354	3·492
1·029 ⎪			
0·853 ⎭	m.s.	0·0339	3·639
0·428 ⎫	f.	0·0308	4·000
0·324 ⎪" b "			
0·262 ⎪			
0·229 ⎭			
K spect. RaB			
K spect. RaC			
0·115 ⎫			
0·099 ⎬" c "			
0·071 ⎭			

Table IX.—μ/ρ of the γ-Rays of RaB and C.
(Determined by Rutherford and Richardson.)

RaB and C.	RaB.
μ/ρ Al.	μ/ρ Pb.
85	4·0
14·7	0·53
0·188	0·18

[*] Rutherford and Andrade, 'Phil. Mag.' (1), p. 869 (1914), and (2), p. 263 (1914).
[†] Rutherford and Richardson, 'Phil. Mag.' (1), p. 722 (1913) ; Richardson, 'Roy. Soc. Proc.,' A, vol. 91, p. 396 (1915).

The value μ/ρ in Al $= 85$ corresponds to very soft X-rays, possibly M characteristic radiations.

The L radiations of bodies of atomic number 82 and 83 have μ/ρ of 17·4 and 16·1 respectively, and so the value found, 14·7, almost certainly represents the combined L radiations of radium B and C, hardened by the superposition of the much less intense group labelled " b "; the group " a " being in the region of the L spectrum would have no effect.

The characteristic K radiations of bodies of atomic numbers 82 and 83 have μ/ρ in Al 0·192 and 0·178 respectively, and in Pb about 4. It can be seen from the Table that values very close to these were found, indicating that the three γ-rays forming group " c " have relatively little energy associated with them.

As Sir Ernest Rutherford[*] has already pointed out, the two groups found by Richardson for radium B having μ/ρ in Pb 0·53 and 0·13 correspond approximately to the γ-rays in the second column of Table IX.

The chief conclusions that may be drawn from this comparison are as follows. Absorption coefficients in aluminium of value greater than about 0·16 are determined mainly by the characteristic X-rays which are excited by the γ-rays. Departures of these values from those of an ordinary element of the same atomic number as the radio-active element indicate the presence of extra radiations not included in the ordinary X-ray spectrum and characteristic of the radio-active element. For instance, Rutherford and Richardson[†] found two groups for thorium B (atomic number 82) for which μ/ρ in Al had values 11·8 and 0·13. Since the K and L radiations alone would give 17·4 and 0·19 there are evidently relatively strong extra radiations of the type labelled " b " and " c " in the radium B γ-rays. It is important to note that the presence of the characteristic K radiations shows the existence of higher frequency γ-rays which eject electrons from the K ring. Hence thorium B and also actinium B with a μ/ρ in Al of 0·165 must emit γ-rays analogous to the main γ-rays of radium B. Such γ-rays could be detected directly by absorption measurements such as Richardson carried out for radium B.

Radium C and thorium D emit a very hard type of radiation having μ/ρ in Al of the order 0·025. The occurrence of β-ray lines of very high energy shows that radium C emits monochromatic γ-rays corresponding to 1—3 million volts in considerable intensity, and these γ-rays probably form part of the hard type of radiation, but it is unlikely that they form all of it since thorium D which emits a slightly harder type of radiation appears to emit no monochromatic γ-rays of energy greater than 800,000 volts. It was

* Rutherford, ' Phil. Mag.,' vol. 34, p. 153 (1917).

† Rutherford and Richardson, ' Phil. Mag.,' vol. 26, p. 937 (1913).

pointed out, however, that thorium D does emit a general distribution of β-rays which extends to very high energies, so the hard type of radiation emitted by thorium D may be "white" γ-radiation of high average frequency emitted as a result of the retardations of these β-particles in their escape from the nucleus. Very little, therefore, at present can be deduced from the detection by absorption measurements of a hard type of radiation. The general results suggest that such a hard type may be either monochromatic γ-rays or "white" γ-rays of high average frequency. or a mixture of these.

Relation of the Characteristic γ-Rays to the Structure of the Atom.

The wave-lengths of these γ-rays depend on the structure of that part of the atom which emits them, and considerable information about this structure can be deduced from the experimental results.

The first point is to settle the origin of the γ-rays. Sir Ernest Rutherford has pointed out on several occasions that the general results indicate that γ-rays are emitted from the nuclei of radio-active atoms, and the numerical values now obtained lend very strong support to this view.

Except as regards the constitution of the nucleus, the radium B atom is identical with the lead atom in every respect. In particular, the K and the L rings, and the fields of force in which they are situated, must be precisely the same in the two atoms, since Rutherford and Andrade found that radium B emits the complete K and L spectrum of a body of atomic number 82. But this last fact indicates something more than this, it suggests that the γ-rays are emitted previous to the actual disintegration of the radium B nucleus, that is to say, previous to the emission from the nucleus of the disintegration electron resulting in the atomic number changing to 83. In fact, it would appear that the γ-ray is emitted, travels out to the L ring, from where it may eject an electron, this electron goes clear of the atom and another electron falls into the vacant place in the L ring, and the nucleus has still not disintegrated.

The main γ-rays of radium B correspond to energies 2·4—4·0 × 10⁵ volts. If they owe their origin to a transition between stationary states in the electronic system of the atom, the end state must be very deep in the atom and certainly inside the K ring, but this possibility is ruled out completely by some work of Chadwick.* He investigated the field of force between the nucleus and the K ring of heavy atoms by observing the deflection of α-particles passing through this region, and he shows that no electrons are present there. Since radium B is identical with lead, except as regards the constitution of the nucleus, this must also apply to radium B. It seems almost certain, therefore, that these γ-rays must come from the nucleus, and

* Chadwick, 'Phil. Mag.,' vol. 40, p. 734 (1920).

since they are emitted previous to the actual disintegration it should be possible to deduce information about the normal radium B nucleus from them.

The main γ-rays of radium B, with their energies, were given in the right-hand column of Table IX. There is a simple arithmetical connection between these energies, the first three being respectively about $1·10 \times 10^6$ volts greater than the last three. If the quantum dynamics holds in the nucleus this arithmetical connection would mean that there were five levels, transition between these levels resulting in the emission of the γ-rays. These levels are shown in fig. 1, with arrows indicating the origin of the γ-rays.
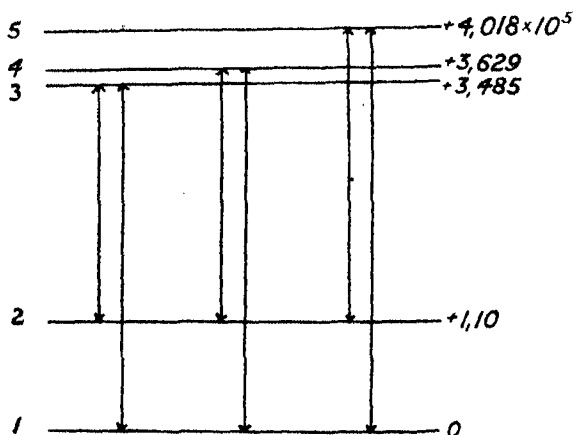
FIG. 1.

But as a necessary consequence of the existence of these levels, there should also be γ-rays corresponding to transitions 5 to 4, 5 to 3, 4 to 3, and 2 to 1. γ-rays corresponding to these energy differences were actually measured by Rutherford and Andrade, by the crystal method, in their work on the γ-rays of radium B and C (see Table IX), and the agreement between the observed and calculated values may be seen from the next Table.

Table X.

Origin.	Energy in volts.	λ in Å.U. (Calculated.)	λ in Å.U. (Observed.)
5–4	$0·389 \times 10^5$	0·318	0·324
5–3	0·533	0·231	0·229
4–3	0·144	0·857	0·853
2–1	1·10	0·112	0·115

The agreement is good and lends support to the view that quantum dynamics apply to the nucleus, and that part at least of the structure of the nucleus can be expressed in terms of stationary states.

If this result be confirmed, it will be of great importance in elucidating the structure of the nucleus, but it would be premature to consider its general bearing at the moment.

The information that has been deduced from these characteristic γ-rays is peculiar in two respects. When it is considered how little is known about the nuclei of heavy atoms, the information that is contained in fig. 1 about the energies of the stationary states of the radium B nucleus is extraordinarily detailed, but, on the other hand, this information is very limited. There is no evidence which indicates whether these levels are occupied by positively charged particles or by electrons, nor is it possible to associate level 5 or level 1 with any special part of the nucleus.

Sir Ernest Rutherford has shown that the emission of the γ-rays is directly connected with the disintegration, but it is very difficult to settle which is the primary phenomenon. This point has been already mentioned· in this paper, but it is important to consider the evidence in more detail, since, if the order were reversed, the levels shown in fig. 1 would probably refer to some system other than the radium B nucleus.

The only argument that can be used depends on the fact that the L spectrum emitted by radium B agrees so well, both as regards wave-length and intensity, with that of lead that it is certain that the L, M, N, ... rings are still identical at the moment of emission with those of a body of atomic number 82. It cannot be asserted definitely, however, that at that same moment the nuclear charge is still 82 units. So little is known about the processes involved in the transition from one stationary state to another that it is possible that there may be a time of relaxation, so that the L, M, N, ... rings of the 82 body may persist for a certain time after the nuclear charge has become 83. If this time of relaxation is greater than the interval between the emission of the γ-ray and the emission of the L spectrum then it is clear that the experimental results are consistent with the hypothesis that the disintegration occurs before the emission of the γ-ray. If, on the other hand, it be assumed that the emission of the γ-ray precedes the disintegration, there is no need to make any hypothesis about the existence of a time of relaxation.

There does not appear to be any more evidence which bears on the question at all,* and so, since the view that the γ-ray comes first is at least *a priori* of

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* It should be noted that on both these views the rate of decay measured by β-rays or γ-rays will be identical provided the average time before the first phenomenon is long compared to the average time between the first and second. The average time before the first phenomenon is the ordinary period, and the general results suggest that either view would fulfil this condition.

equal probability as the opposite view, and since, in addition, it does not involve any extra hypothesis about a time of relaxation, it will be assumed provisionally to be true.

There are several consequences that result from this decision. Firstly, the levels shown in fig. 1 can be assigned to radium B, and they are considered to represent the normal structure of the nucleus. Secondly, the general picture of a β-ray transformation is different from that which one would make if the disintegration were to occur first. This last case has already been treated by Sir Ernest Rutherford; the result of the alternative view may be illustrated by considering the radium B tranformation.

The radium B nucleus comes into existence after the α-particle has left the radium A nucleus, but one would not anticipate that all the radium B nuclei were absolutely identical. The particle which does the transitions between the levels of fig. 1 will be in one of these levels, but it need not be in the same level in each nucleus. Subsequently, during the life of the nucleus this particle passes to another energy level with the emission of a γ-ray. Finally, the particle will arrive in one of the states which is connected with instability, and the nucleus disintegrates with emission of an electron.

This view suggests a clear distinction between the γ-ray and the β-ray lines, on the one hand, and the continuous β-ray spectrum, on the other. The former are characteristic of the normal life of the nucleus and give information about its structure. The latter is characteristic of the disintegration of the transition of one element to another and is analogous to the α-rays.

An interesting point arises from the consideration of energy levels in the nucleus. In Table VIII, showing the γ-rays of radium B and C, there are two groups labelled "b" and "c," whose wave-lengths do not coincide at all with either the K or the L spectra, yet the wave-lengths are of a magnitude that, in the absence of other evidence, would indicate their origin to be somewhere in the electronic structure of the atom, whereas all X-ray evidence goes to prove that there are no other states besides the K, L, M, etc. Four of these lines have been accounted for in the above Table, and it is reasonable to suppose that the remainder originate in the same way, in either the radium B or radium C nucleus.

Too few γ-rays of radium C have been identified for it to be possible to obtain independent evidence about the existence of nuclear levels, but it is interesting to note that if the γ-rays that have been measured are fitted into a set of levels, this set would also give γ-rays which, on conversion in the K ring of radium C, would give β-ray groups agreeing with Rutherford's measurements.

The measurements of the γ-rays of thorium D, however, are sufficiently detailed to give strong confirmation of the hypothesis about stationary states in the nucleus. A set of eight stationary states is postulated, consisting of four groups, the energies being 0·41 and 0·56 × 10^5 volts, 2·28, 2·48, 2·54, 2·74 × 10^5 volts, 5·11 × 10^5 volts, and 9·02 × 10^6 volts. This set of levels gives the ten γ-rays actually measured, and in addition gives eight more γ-rays which, on conversion in the K ring of thorium D, would produce β-ray groups agreeing with those measured. This result may be stated another way by remarking that this set of levels would give γ-rays which would account for thirty-three out of the thirty-seven β-ray groups actually measured.

The general results lend strong support to the view that stationary states exist in the nucleus, and it is hoped that by investigating the γ-rays of other radio-active bodies, some general principles in the arrangement of nuclear levels may be found.

Summary.

1. A general method for measuring the wave-length of γ-rays is given.

2. The analysis of the β-ray emission of radium B has been completed.

3. The lower energy section of the radium C β-ray spectrum has been analysed by the excited spectrum method and the γ-rays found.

4. The β-ray spectrum of thorium D has been measured and the effective γ-rays deduced.

5. It is shown that it is very probable that the γ-rays of radio-active bodies are emitted from the nucleus.

6. Evidence is brought to show that the quantum dynamics applies to the nucleus, and suggestions for the arrangement of the nuclear levels of radium B and thorium D are given.

Suspended Impurity in the Air.

By J. S. OWENS, M.D.

A study of the impurity in the air involves the measurement of quantity as well as the provision of means whereby the nature of the suspended matter can be examined. The object which the author had in view in making this investigation was to provide some simple and effective method for examining the quantity and nature of suspended dust, and its relation to visibility, fumes from industrial processes, dust produced in mines, fogs such as are experienced in our larger cities, and generally in the hope of throwing some light on problems which are concerned with the presence of fine suspended impurities in the air.

This paper is devoted chiefly to a description of a method of trapping for examination the suspended matter in the air, and the application of the method, and also to a discussion of the relation between dust and visibility. The work described by the author was carried out for the Advisory Committee on Atmospheric Pollution. This Committee has as its function the obtaining and consideration of data upon atmospheric impurities. The methods adopted fall into two distinct groups—the measurement and examination of :—

(a) Matter deposited from the air ; and (b) Matter suspended in the air.

Filter Paper Method.

In order to measure the suspended impurity, a method was used in which a fixed volume of air, filtered through white paper, left a mark on the paper, the shade of which indicated the quantity present. This method owed its practicability to the fact that the suspended matter in city air is mainly derived from smoke and is thus black in colour, and the particles fairly uniform in size, so that in practical use it has been found that the discoloration as measured upon a scale of shades gives a reasonably accurate measurement of the quantity of impurity present.

An automatic instrument, operating on these lines, and designed by the author, has been in use by the Committee for some time, and as it gives automatically three or four records per hour, night and day, it provides a means of comparison of the quantity of impurity present at different hours.* · The instrument has been fully described elsewhere, and as a result of its use

* 'Fourth Annual Report, Advisory Committee on Atmospheric Pollution.'

the suspended impurity in London and other cities where it is in operation has been shown to vary in a certain definite way. From midnight to about 6 A.M. it is a minimum, then rises rapidly to a maximum at about 10 to 11 A.M. on week-days and 12 noon on Sundays, after which it falls off. There is usually a slight rise about 5 P.M., and about 10 P.M. it drops rapidly till midnight. Thus there is a regular daily cycle. As stated above, this instrument is limited to the measurement of impurities which are sufficiently black for comparison with the standard scale. It is also open to the objection that the dirt trapped, being entangled in the meshes of the filter paper, cannot be subjected to microscopical examination.

Other Methods.

Many other methods of determining the amount of dust in the air have been used, perhaps the best known being the Aitken* dust counter, in which a measured volume of air is drawn into a small dust-free chamber, and by reducing the pressure within this chamber a deposit of moisture is brought about, the particles settling on a glass floor, where they can be counted. The assumption is made that each drop of moisture condenses round a dust particle; but this assumption cannot be justified, as condensation is known to occur in the absence of dust. Methods of filtration through soluble filters have also been used, such as collodion wool; these are subsequently dissolved in ether and the particles in a small measured volume counted (Hahn), or filtering through sugar and subsequently dissolving it in water. Methods such as these, in which the dust particles are ultimately suspended in a liquid, are clearly objectionable, as some of the suspended particles may be soluble in the liquid; also the particles composed of aggregates of finer pieces would tend to get broken up in the liquid, so that it is hardly justifiable to assume that the number obtained from the liquid suspension is a fair measure of the number suspended in the air.

The method of ascertaining the quantity of suspended matter by filtering a measured volume of air through weighed paper or other filter, and subsequently re-weighing is extremely difficult to apply, as the normal weight of impurity present in fairly dirty city air is of the order of 1 mgrm. per cubic metre, while a dense smoke fog contains approximately 4 mgrm. per cubic metre. Hence the filtration of large volumes of air would be necessary to get weighable quantities, and the time required for the filtration of such volumes precludes the possibility of ascertaining the state of the air by this method at any particular time. The automatic instrument above referred to was calibrated by using this method; that is, large volumes, amounting to

* 'Trans. Roy. Soc. Edinburgh,' vols. 30–36.

over 1000 cubic feet of air were filtered through discs of thick filter paper, in order to get sufficient quantity to weigh without too great an error.

A method has been used by G. T. Palmer* in which a quantity of air is drawn through a water spray, the number of particles in a measured quantity of the water subsequently counted, and the weight ascertained by evaporating and weighing the residue. This method obviously depends on the wetting of the dust particles by the water. It has been examined critically by Katz, Longfellow and Fieldner† with the result that the efficiency of the apparatus for stopping tobacco smoke is given as 13 per cent., while for fine silica powder suspended in the air the efficiency was 30 per cent. when the air was drawn through at 4 cubic feet per minute, and 20 per cent. at 3 cubic feet per minute, as examined by a light test. When examined by the weighing test the percentage of impurity stopped, when air was drawn at 4 cubic feet per minute, is given as 45.

It is extremely difficult to wet dry dust, and an apparatus depending on the wetting of dust particles by a spray is not likely to be very efficient. In this connection it may be of interest to observe that in the records of deposit obtained at the Committee's stations in different parts of the country, it has been found that while the deposit of atmospheric impurities which are soluble in water varies almost directly with the rainfall, there is no such relation between deposit of insoluble matter and the rainfall.

The exposure of plates or dishes to the air for a definite time has been used with a view to ascertaining the amount of dust in the air, but all such methods measure only deposited matter and consequently give no information as to the amount of dust suspended in the air. Speaking generally, any method which requires a long time for its application is of little use when the quantity of impurity in the air is subject to rapid variation.

Jet Apparatus.

The following method of obtaining a sample of dust from the air for measurement and examination has been evolved by the author, with a view to microscopic examination of the dust and in order to get an instantaneous value of the quantity of impurity.

A very small jet of air is made to impinge upon a glass surface, such as a microscope cover-glass, at a high velocity, under suitable conditions, when the dust suspended in the air carried in with the jet adheres to the glass and a record is obtained which can be removed and examined microscopically. In the first apparatus made the air jet was obtained by drawing air

* 'Amer. J. Pub. Health,' vol. 6, p. 54 (1916).
† 'Journ. Industrial Hygiene,' vol. 2, No. 5, p. 167.

out of a small cell, the floor of which was perforated by a round hole 0·15 mm. diameter, the roof being formed by a cover-glass at a height of 0·8 mm. above the floor. By making the floor of the cell out of a sheet of mica it was possible to observe the operation of the jet under the microscope.

On watching the cover-glass through a ¼-inch objective while air was drawn out of the cell, dust particles could be watched striking and sticking to the glass, and many of them were noted to be in the middle of small drops, presumably of water. The sensitiveness of this apparatus was so great that by clipping the end of an ¼-inch rubber tube communicating with the cell, pinching it between the finger and thumb, and then releasing it, a shower of dust particles was seen to strike and adhere to the cover-glass. The amount of air drawn through the jet thus was subsequently ascertained to be 0·15 to 0·18 c.c.; and the number of dust particles which struck the glass from this quantity of air was about 30, the test being made on a fairly clear day at Cheam, in Surrey, inside a room.

This apparatus had certain objections as, owing to its extreme sensitiveness, a very small volume of air only could be used and this might not be representative. Again, the size of the record obtained was so small that it was very difficult to find under the microscope, unless observed at the time of taking. This apparatus, when run in series with a paper filter, was found to be very effective in trapping the dust, a small proportion only escaping. In a test made in London in this way, two litres of air were drawn through the jet apparatus and then through a filter paper, and on subsequent examination a small pinnacle of black dirt was found deposited on the cover-glass immediately opposite the jet; this was about 0·2 mm. high and consisted of an almost perfect cone with its base on the glass. The conditions of impact of the dust particles, therefore, were altering during the test, starting by impact on a plane glass surface and finishing with impact upon the point and sides of the cone; thus the test made in this way was not regarded as a satisfactory one of efficiency, although it indicated that most of the dirt was removed from the air by the jet.

In a subsequent apparatus the hole for forming the jet was produced by cementing the two halves of a cover-glass, the edges of which had been ground smooth, over a hole formed either in a brass disc or in another cover-glass. This hole varied in diameter from 2 up to 11 mm., and the glass edges formed the sides of a slot and were adjusted to a distance apart of 0·1 mm. Thus the hole consisted of a long slot, 0·1 mm. wide and from 2 to 11 mm. long. This is shown in Fig. 1.

By using a jet formed by a slot of this type several advantages were

gained :—It was possible to find the record on the cover-glass after removal
from the apparatus; also the volume of air used in taking the record could
be increased and so made more representative. The
actual volume used with a slot 11 mm. long, in
London, is about 50 c.c., but the volume required
depends upon the quantity of impurity present at
the time; as it is essential that, for purposes of
counting, the dust particles should not be too
numerous. The number can then be ascertained by
using a net-ruled micrometer eye-piece in the micro-
scope.
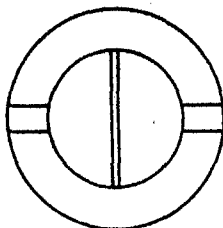
Fig. 1.

It is somewhat difficult to find a method of test-
ing the apparatus for efficiency, but an arrange-
ment was ultimately designed and made, as shown
in fig. 2. Two cells were provided instead of one, the bottom cell had a
slot, B, in its floor a little to one side of the centre. The floor of the bottom
cell was formed of the two halves of a cover-glass, cemented to a flat brass
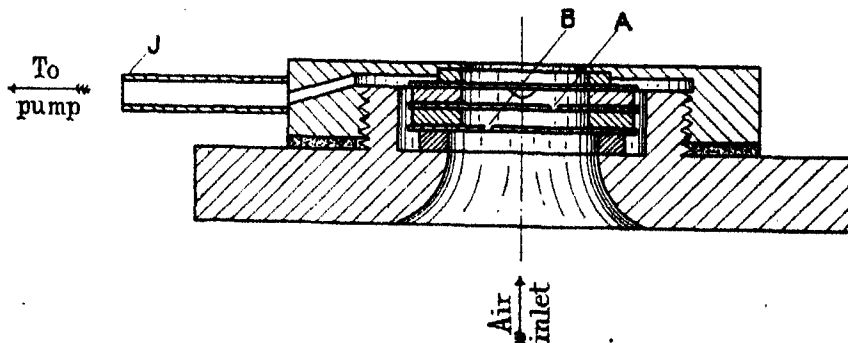
Double cell
Fig. 2.

ring to form the slot, the edges of which were ground smooth and straight.
The roof of the bottom cell was similar to its floor, but had a slot, A, upon
the opposite side of the centre. The roof of the upper cell was formed of a
cover-glass, and each cell was 1 mm. deep. This apparatus could be placed
upon the stage of the microscope and kept under observation while a record
was taken. The tube J communicated, through the annular space around
the top cover-glass, with the upper cell; the joint between the roof and
floor of the lower cell was made air-tight. By drawing air from the upper
cell it entered through the slot B in the floor of the lower cell, the jet
striking the roof of that cell, and the air then passed through the slot A

in the roof of the lower cell, the jet striking the roof of the upper cell. Thus, if all the dust in the air were trapped in the lower cell, no dust would appear upon the top cover-glass, also if a suitable volume of air be drawn through, the number of particles upon the cover-glass forming the roof of the upper cell, compared with the number upon its floor, would give an indication of the efficiency of the jet. The apparatus was made and used in order to ascertain the efficiency of the jet, and also to determine the most suitable size of orifice to use. The results so far indicate that under suitable conditions, the first cell traps practically all the dust particles.

If the percentage of the total caught by the jet is less than 100, but remains constant, then let :—

T equal the total number of dust particles in the air drawn in.

C_1 equal the number caught on roof of first cell.

C_2 equal the number caught on roof of second cell.

Since C_1 and C_2 bear the same ratio to the number in the jet

$$\frac{C_1}{T} = \frac{C_2}{T - C_1}.$$

Therefore

$$C_1 T - C_1{}^2 = C_2 T \qquad \text{and} \qquad T = \frac{C_1{}^2}{C_1 - C_2}.$$

Thus the total T can be found. Similarly, if the proportion of the total which is caught is constant, this proportion can be found once for all from the observed value of C_1 and calculated value of T, *i.e.*, C_1/T.

The following Table gives a few values of efficiency as calculated from the above method :—

Volume of Air Aspirated in each Test = 1000 c.c.

Experiment number.	Count per strip across record.		Efficiency percentage of jet calculated from the formula $T = C_1{}^2/C_1 - C_2$.	Velocity in jet in metres per second.
	Top cell.	Bottom cell.		
1	148	816	82·5	Approx. 90
2	258	700	63·6	,, 90
3	95	500	81·0	,, 90
4	170	1200	81·4	,, 90
5	300	1200	75·0	,, 90
6	160	338	52·7	,, 90

This method of testing is not quite satisfactory, as the conditions are not the same as when a single jet is used. The resistance of the two slots probably reduces the velocity below that in the single-slot apparatus, and, as

shown later, the efficiency falls off rapidly as the velocity is reduced. It is probable, therefore, that the actual efficiency is higher than indicated by the double-cell method. A convenient method of drawing the air through the jet is by means of an air-pump having a displacement of 50 c.c.

By testing with the double cell above described, it was found that the most efficient diameter of circular hole was about 0·15 mm.; for example, a jet 0·076 mm. in diameter trapped a lower percentage of dust particles. In the case of the slot-shaped holes it was found that about 0·10 mm. was the most efficient width; for example, reducing the width to 0·04 mm. gave a less efficient result.

A curious phenomenon was noticed in the test for efficiency above described. Occasionally the second cell collected no particles whatever, that is, all were trapped in the first; while at other times about 30 per cent. of the particles penetrated to the second. A test on October 26, during a smoke fog in London, gave 100 per cent. efficiency, i.e., all the particles were trapped in the first cell. There appears, therefore, to be some variable condition which affects the adhesion of the particles, and from subsequent experiments this condition appears to be the humidity of the air; an attachment was therefore made by means of which the air was made to approach the jet through a damp-walled chamber in order to raise the humidity and keep the air as nearly saturated as possible. The tests of efficiency here given were made without the moist chamber.

Another method for examining the efficiency by means of the double cell has been applied; that is, a record was taken with the double cell and counts made; then, using the formula given on page 23, the total number of particles calculated. A second record, taken at the same time with a single cell, was then counted and the result compared with the total obtained as above described. By this method a figure was obtained which agreed well with the values of efficiency already given. The numbers in one particular experiment were as follows :—

Number of particles per cubic centimetre from count of record in single cell, 620.

Number of particles per cubic centimetre from count of record in double cell, 756.

Efficiency from these figures = 82 per cent.

When observing the action of the double cell it was clear that only the finer particles escaped from the lower cell, and not many of these. The efficiency, as estimated from counting, would therefore be lower than if estimated on a weight or volume basis.

In an attempt to estimate the efficiency by comparison with a count of particles using an ultra-microscope, it was found that the number of particles as counted under the microscope, while in suspension, was much less than the count obtained from the jet. The ultra-microscopic method is subject to the objection that an extremely small volume of air is used, and it may not be representative; but this result suggests also that the visibility of the particles may be reduced while in suspension owing to Brownian movements.

The final form of the jet apparatus is shown in fig. 3. The apparatus consists of a brass sleeve B, into the upper part of which is screwed a plug C, which makes an air-tight joint with the sleeve by means of a leather washer H. Into the lower opening of the sleeve is screwed a brass piece K, perforated by a funnel-shaped hole, varying in diameter at its narrowest place from 2 to 10 mm., according to the length of the slot to be used. The slot for forming the jet is shown at A and is formed by a diaphragm of hard brass or copper-sheet in two half-discs, the straight edges of which form between them the slot. This diaphragm is held in place by a brass ring by means of four screws which permit the setting of the slot to the correct width. This brass ring is of suitable diameter to receive a ¾-inch cover-glass in a recess formed upon its upper surface, and it is perforated by a central hole of the same diameter as that in K; thus a slot is formed the length of which is determined by the diameter of this hole. In order to hold the cover-glass in position over the slot a spring washer D is fixed upon the lower end of the plug C. A connection E is fixed on the side of the sleeve B for an air-pump, of suitable capacity, usually 50 c.c.

To the outer part of K is fixed a thin brass tube T, of a capacity of about twice that of the air-pump. This tube is lined with blotting-paper U, held in place by two wire rings. Before taking a record this blotting-paper is saturated with water, the function of which is referred to below. This makes a convenient form of apparatus and its sensitiveness can be adjusted by using slots of different lengths, but for use in city air a slot 1 cm. in length is found suitable, the volume of air used being 50 c.c. When in very clean air a shorter slot, say 2 mm., may be used, or a greater volume of air drawn through.

Flow of Air in Jet.

The velocity of flow of air through an orifice is a function of the difference in pressure between the two sides of the orifice, but has a limiting value when the pressure on the low side is 0.527 of that on the high, the maximum velocity obtainable being the velocity of sound in the jet. The velocity of sound in dry air at $0°$ C. is 3.3133×10^4 cms./secs. and through a jet 2 mm. long and 0.1 mm. wide, measured approximately by taking the time required

to pass 50 c.c., was about 2.5×10^4 cms./secs. Thus it is approaching the limiting velocity, and is of a very high order, being, in rough figures, about.

Section

Plan with plug C removed
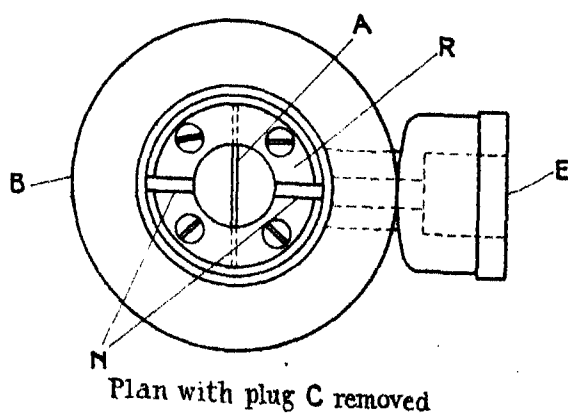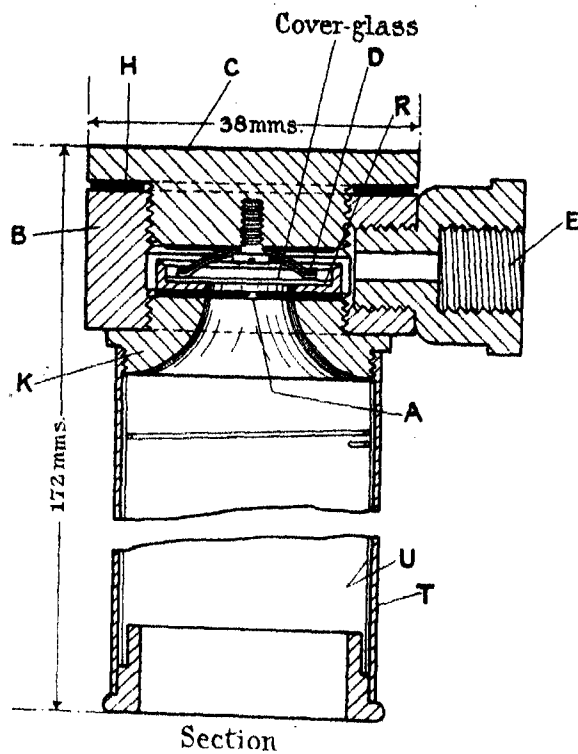
Fɪɢ. 3.

10 miles per minute. As the velocity was measured at atmospheric pressure, if account be taken of the expansion due to fall of pressure in jet,

it is probable the true velocity is equal to that of sound. The particles of dust which are drawn through with the jet, therefore, travel at an exceedingly high velocity, and when the jet is deflected on striking the plate, these particles are projected against the glass, where they adhere.

Adhesion of Dust Particles to Glass.

Why dust particles projected against the glass should adhere is not very obvious, but certain explanations suggest themselves; for example, to produce the jet the air in the cell has its pressure reduced and there is a fall of pressure in the jet, due to the high velocity; this doubtless results in moisture being condensed around some, if not all of the dust particles at the moment, or just before the moment, of striking. That this action does take place is obvious on watching the process through a microscope, as some of the particles can be seen surrounded by water. This is the same effect as is produced in the Aitken dust-counter, but the quantity of moisture so condensed is extremely small and, when the cover-glass is removed from the apparatus for counting, it evaporates rapidly; thus there need be no confusion over the counting of water drops as dust particles.

The function of the tube T is to saturate the air with water before it is drawn through the jet. In operation two or three pumps-full of air are drawn in before the cover-glass is placed in position, thus filling the tube T, with air to be tested. The cover-glass is then placed in position in its recess over the slot, the plug, C, screwed home, and 50 c.c. of air are drawn through the slot as rapidly as possible.

It was found in experimenting with this that if the tube T were held in the hand so as to be slightly warmed, a visible mist appeared in the tube, and a record taken under those conditions was spoiled by the water drops washing away the dust in streams, and thus making it impossible to count. When, however, the tube is kept cool so that no visible mist is formed this difficulty does not arise; it has been found that the addition of the tube makes the apparatus more efficient. It seems probable in the light of this that some of the variations in the amount of dust shown in Table I were due to variations in moisture-contents, as the jet used had not the attachment referred to. Owing to the great variations noticeable between records taken with and without the tube T, there appears to be little doubt that the chief cause of adhesion of the dust particles is condensation of water upon them as they pass the jet and the pressure is suddenly reduced.

As bearing upon the effect of the velocity of the jet it appeared possible that there might be an observable effect if the velocity could be varied, and to examine this several experiments were made in which air was drawn through

the jet at different rates, other conditions being the same, and the number of particles adhering to the glass counted. The results of these tests were as follows :—

Jet used—2·42 mm. long by 0·135 mm. wide.

Experiment number.	Volume in c.c.	Time of flow in seconds.	Average count per square.	Method of aspirating.	Approximate number of particles per c.c. calculated from count.	Velocity through jet in metres per second.
(a)	50	1	100 (estimated)	Pump	140	160
(b)	78	10	34	Gas burette	81	25
(c)	62	15	10	,, ,,	11	13·1
(d)	50	1	100 (estimated)	Pump	140	160
(e)	83	10	26	Gas burette	22	26
(f)	78	20	14	,, ,,	13	12·5

It appears certain, therefore, that the velocity of the jet has a profound effect upon the result obtained, and it is necessary to keep the velocity as high as possible in order to get the greatest efficiency. In view, however, of the condensation effect referred to above, it is possible that some of the results attributed to varying velocity may be due to the fact that a low velocity implies a small reduction of pressure, whereas a high velocity implies a greater reduction, and thus the condensation of water may be dependent upon the pressure.

A somewhat curious phenomenon, the cause of which is not yet very obvious, is the occurrence of flocculated masses on the records. When the air is drawn through the jet at a low velocity (about 7 to 8 metres per second) the records consist sometimes of practically nothing but masses of particles collected together in lumps; these are referred to in Table I as aggregates. A record taken at the same time, using a high velocity of about 170 metres per second, showed practically no aggregates and consisted entirely of fine particles scattered uniformly. This appears to indicate that the aggregates are formed in the jet and do not exist in the air before aspiration; it also suggests some electrical effect, perhaps due to the rapid flow in the jet.

Application.

Visibility and Dust.—It appears probable from the tests already made by the author that the presence of suspended dust in the air is one of the chief factors governing visibility on occasions when there is no fog to obliterate vision at short distances. On several occasions when the visibility was bad, and a distinct grey or bluish haze was seen against distant objects, tests taken

revealed the presence of abnormally large numbers of dust particles. During last August, while on a holiday in Norfolk, samples of the air were taken daily and the relation of the quantity of dust to the visibility roughly estimated. With the exception of August 25, not yet accounted for (probably due to variation in relative humidity), and another day when there was a water mist, the visibility appeared to be a function of the number of suspended particles. It would seem, therefore, that there is a useful field of application in attempting to relate the quantity of suspended matter with visibility.

Expired Air.—Another application of the apparatus is to the examination of expired air, with a view to ascertaining whether the suspended impurities in the air breathed are retained or expelled. Experiments made on this indicate that the tidal air expired contains a large proportion of the suspended matter which was inspired, while the " reserve " air from the deeper parts of the lungs, while containing very much less than the tidal air, still does contain some of the suspended matter breathed in. An important result obtained was that the quantity of dust in the deep parts of the lungs depended chiefly upon the nature of the breathing, that is deep breathing from any cause carried dust into the deeper parts, and even the last part of reserve air under such conditions was found to be laden with dust.

Examination of Fumes, Mine Dust, etc.—As a means for rapidly sampling fumes from different sources for microscopical examination, the jet arrangement should be useful. The same applies to mine dust, or dust from other sources ; the chief points of advantage being the possibility of instantaneous sampling of the air, and the fact that the records obtained can be preserved for future reference, while the dust particles are not acted on in any way, such as by suspension in liquid which precludes the possibility of measuring soluble dust.

Vertical Distribution.—The examination of the vertical distribution of suspended matter in the air is another use to which this apparatus may be put. The whole apparatus is very small and light, and the records can be taken in a few seconds, so that it would be a simple matter to take it up in an aeroplane or balloon and obtain samples at different heights, preserving the records for examination later.

These are a few of the applications which suggest themselves at the moment; and, as illustrating the use of the jet, a description will be given of an examination of the suspended impurity and its relation to visibility and wind direction.

Transport of Suspended Impurity by the Wind.

It is well known that the chief source of suspended atmospheric impurities in this country is the burning of smoky fuel. The seasonal variation is very well marked, the quantity of impurity falling off to a minimum in the summer and rising to a maximum in the winter, when all the domestic fires are in full operation. There is a similar relation in the hourly variation, the only period comparatively free from smoke pollution being the small hours of the morning when fires are out. The distance to which smoke impurities travel from their source is not known.

For some years the author has noticed that when the meteorological conditions were suitable, usually in anti-cyclonic weather, with gentle easterly or north-easterly winds, it was usual to find a bluish haze overlying the whole country. By the aid of the filter already mentioned, this haze was found to be composed of solid particles which gave a distinct discoloured record on the white filter paper. It is a matter of conjecture where these particles come from, but the author would hazard the statement that they are often derived from the smoke of Continental fires. From observations made during last August, it appears highly probable that the great industrial effort now being made by Germany is, under certain conditions, responsible for a fair proportion of the suspended impurity in the air over this country. The method of observation on which this statement is based was as follows :—

Records of suspended dust were taken daily on the coast of Norfolk during last August, close to the edge of the sea. The records were preserved, also careful notes of the wind direction and velocity each day. The Daily Weather Maps issued by the Meteorological Office, indicated the wind direction over a large area, and thus the direction from which the impurity came.

The results of these experiments are set forth in Table I.

All the records tabulated were taken at Holme, Norfolk, on the sea coast, the exact position being indicated in the Table, but in no case was the distance from high-water mark more than 150 yards, the intervening space being covered by marram grass and fir trees, so that there was no source of dust.

Volume of Air.—The volume of air drawn through the jet was varied from 100 c.c. up to 1000 c.c., the smaller volume being used with the hope of being able to make a count of the particles.

Visibility.—The figures given for visibility are those for Pulham, which was between 40 and 50 miles away, and therefore the conditions were probably not the same as at Holme, where the records were taken; the figures are inserted as having been taken by a skilled observer at the Meteorological

Table I.—Records of Dust Suspended in the Air taken at Holme, Norfolk, August, 1921. Jet Apparatus.

Date (August, 1921).	Conditions of Observation.				Time (G.M.T.).	Volume of air used.
	Place.	Weather.	Visibility at Holme.	Visibility at Pulham at 18 h. M.O. code.		
13	Land side of sand hills	Blue haze, sunny, some clouds, thunderstorm 14 h.	—	7	h. 14	c.c. 200
13	Low-water mark	Blue haze, sunny, some clouds, thunderstorm 14 h.	—	7	15	1000
18	Sand hill	Sunny, haze, thin cirrus clouds	Sea horizon invisible	8	11¼	200
18	„	Sunny, haze, thin cirrus clouds	„	8	17	100
19	„	—	Sea horizon invisible 10 h., just visible 19 h.	9	12¼	100
20	Edge of sea	Fine, sunny, cirrus clouds, heavy haze	Sea horizon invisible	8	12¼	100
24	Sand hill	Damp, overcast	—	5	16¼	1000
25	„	Sunny, slight haze		7	19¼	500
26	„	Very little haze	—	9	16¼	Up to 1000
27	Land side of sand hills	Sunny, haze nearly gone	Good	9	16	1000
27	Sand hill	„	„	9	16	1000
28	„	Very little haze, sunny; light cirrus from S.	Very good; Skegness visible, also sea horizon	8	16¼	1000
29	„	Bright sun, clouds, marked haze	Sea horizon just visible, not Skegness	8	13	100
30	Water edge	Cumulus, sunny intervals, some haze	Skegness just visible	8	13¼	1000
31	Land side of sand hills	Sunny; light cirrus from W., dense haze	Very bad, sea horizon invisible	8	10¼	1000

Table I.—(continued.)

Microscopic Examination of Suspended Particles.

Date (August, 1921).	Method of mounting.	Slide number.	Number per c.c. from count under microscope.	Number corrected for loss in Canada Balsam.	Range of shape and size.	Average diameter.	Nature of particles.
					microns.	microns.	
18	Canada Balsam	1	65	150	0·85–0·34	0·5	No crystals, no aggregates; fine dark-coloured dust.
18	"	5	Over 200 (too many to count)	—	1·70–0·34	0·5	No crystals.
18	"	8	72	168	1·40–0·34	0·5	Very uniform in size; no crystals, no aggregates.
18	"	13	133	310	1·40–0·34	0·5–0·7	Very uniform in size; no crystals, no aggregates.
19	Dry	19	100	—	0·85–0·34	0·5	Rounded; no aggregates, some crystals.
20	"	22	145	—	1·40–0·34	0·5	Some crystals, no aggregates.
24	Canada Balsam	26	90	70	1·70–0·85 (Spheres grading to 0·34)	0·5	Some spherical.
25	"	28	130	304	1·70–0·34	0·5	All rounded; some perfect spheres.
26	"	33–37	Not enough to count	—	—	—	
27	"	41	12	28	Spheres 1·4 (grading to 0·34)	0·5	All rounded; very variable in size.
27	Dry	41	28	—	1·4–0·34	0·5	No crystals, all rounded; large spheres grading to smallest particles.
28	Canada Balsam	43	—	17	Up to 1·7	0·5	Irregular in size and shape; a few aggregates.
29	Dry	48	196	—	Spheres 1·7–0·85 down to particles 0·34	0·5	Big; rounded and very variable in size; some drops.
30	"	52	34 (excluding drops)	—	1·7 (grading to 0·34)	0·5	Very variable in size; many drops present, crystallising on standing.
31	"	55	Over 200 (too many to count)	—	Max. 2·55 (grading to 0·34)	0·5	Very variable in size; some spheres; many aggregates.

Table I—(*continued*).

	At ground level.			At 1000 feet.
Date (August, 1921).	Holme at time of taking records.	Pulham at 13 h.	Pulham at :— 18 h. Near time of taking records.	Pulham near time of taking records.
	mi/hr.	mi/hr.	mi/hr.	mi/hr.
18	W.	0 0	W. 1-3	15
18	—	—	—	—
18	N.E. 8·5	E.N.E. 13-18	E.N.E. 15	24
18	N.E. 12·8	—	10	12
19	N.N.E. 12·8	E.N.E. 19-24	N.E. 13	13
20	N.E. 12-14	N.E. 8-12	— 5	7
24	N.-N.W. —	N.N.W. 8-12	N.E. 8-12	3 (at Howden).
25	W. —	W.'S. 8-12	W. 10	15
26	S.W.'W. 10-13	W. 8-12	W.'S. 8	13
27	W.* —	W.'S. 13-18	S.W. 20 (Howden at 17 h.)	30 (at Howden).
27	W.	—	—	—
28	N.-N.E. 0-8	0 0	E.N.E. 6 (at 11 h.)	10 (at 11 h.).
29	W. —	W.'S. 19-24	W. 25	31
30	N.N.W. 12-15	N.N.W. 8-12	W.'S. 6 (at Cranwell)	10 (at Cranwell).
31	W. light —	W. 8-12	S.'E. 7 (Cranwell at 12 h.)	14 (Cranwell at 12 h.)

* Had blown all night from S.W.-W., *i.e.*, Hunstanton—4 miles away.

Office Station at Pulham and published in the British Daily Weather Report. Rough observations of visibility were also made at Holme, as referred to later.

Method of Mounting.—The records obtained were mounted on microscope slips and preserved for subsequent examination. The method of mounting, however, was not always the same; some of the earlier records were mounted in Canada Balsam, but the later ones were mounted dry, as it appeared possible that the balsam might affect the record and make the subsequent counting incorrect. As a matter of fact this was found to be the case, and the records mounted in balsam always gave a very much lower count than they should have done. This was ascertained to be due to the balsam, by examining some records part of which were mounted dry and part in balsam, also by observing the behaviour under the microscope of a record which was mounted dry, and balsam allowed to flow in under the cover-glass. In order to correct for this, as far as possible, an estimated figure is given for the records mounted in balsam obtained by multiplying the actual count by 7/3, which was found to

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be about the ratio of particles mounted dry to a count of a record taken at the same time and mounted in balsam.

The number of particles per cubic centimetre of air is based upon a count under the microscope, and is not to be taken as absolutely correct, but rather as a minimum figure, since the counts were made of particles adhering to the glass of the jet apparatus and no allowance made for those which may have escaped; the latter were, however, probably not over 20 per cent. The damp approach-chamber was not in use at this time.

Wind.—The wind direction as observed at Holme is given, and also as observed at Pulham. Where the velocity at Holme is given it was measured at about 6 feet above the ground, by means of thistledowns timed over a length of 50 yards of smooth sand. As the wind direction was measured near the surface and the records taken near the surface, while the chief source of suspended impurity is also probably fires situated near the ground, it would seem that it is the wind near the surface which is to be considered the transporting agency. The vertical distribution of suspended matter is unknown at present, but it appears probable that most of the suspended matter is held within 200 or 300 feet of the ground. The wind velocity at 1000 feet is given for Pulham for comparison with the surface wind, the figures being taken from the Daily Weather Report.

The diameters of the dust particles given in Table I were measured by means of an eye-piece micrometer, using a 1/12-inch oil immersion objective, having a numerical aperture of 1·28. The limit of resolution for such an objective, based upon Airy's theory, would be about 0·216 micron, that is all particles of this size, or lower, would appear of the same diameter.

The average size of the particles as given in Table I, was about 0·5 micron and therefore well above the limit of resolution, so that when uniformity in size was noted, this uniformity was not the result of particles falling below the limit of resolution and producing spurious discs.

All records taken during the west winds showed a number of small spherical particles, which were completely absent during the north-east winds. These spherical particles were not uniform in diameter but varied considerably, from nearly 2 microns down. It is possible that they may have been fused ash particles, but if so they should be dense, and one would have expected them to settle more rapidly than the smaller, and more irregularly shaped, grains. It is of interest to note in this connection that small spherical particles are very common in the flue dust from boiler furnaces and are especially numerous in furnaces using pulverised coal.

The Sources of the Impurity Observed.

The results exhibited in Table I have been considered with reference to a journal of the direction and velocity of the wind at 13 h. and 18 h., at Pulham, in Norfolk, 40 miles to the south of Holme, and at Cranwell, in Lincolnshire, about the same distance to the west, from August 8 to August 31. Taken in conjunction with the local observation it gives a fair general idea of the distribution of the surface wind. The journal was computed from the British Section of the Daily Weather Report and need not, therefore, be reproduced here, but may be referred to in support of the provisional conclusions derived from the observations.

On August 13, after a change from E. to N.W., the wind was due W., blowing across the Wash to the point at which the sample was taken. The suspended matter in the air was, therefore, probably derived from the industrial centres of Yorkshire or the Midlands. In the evening of Wednesday, August 17, after a spell of southerly winds which terminated with a thunderstorm followed by a remarkably clear atmosphere, a wind set in from the east with a marked haze, and settled into N.E. for three days with persistent dense haze. On the 18th, two samples were taken in north-easterly wind which had blown into the Wash from the North Sea, and touched land first at the point of observation. The number of particles in the evening sample was greater than in the morning. The north-east wind and the haze continued for the 19th and 20th, but on the 19th a shift of wind more to the east with an increase of strength produced less haze. The wind was remarkably constant, both at Pulham and Cranwell, and the velocity was sufficient to carry the air over 1,000 miles in the three days. Leaving out of account the effect of passing steamers, as being out of the question, there appears to be no source of the suspended matter on this occasion except the Continent, and we may fairly conclude that it crossed the North Sea.

Between August 21 and 24 the wind got away to northerly or north-westerly with a relapse to N.E. on the 22nd, reverting to N. on the 23rd and N.W. on the 24th. There was thick haze all the time, becoming thick damp fog on the 23rd. No observations were made during the northerly weather for want of material, but in the N.W. wind of the 24th the observations were resumed and a new feature was disclosed. There were apparently spherical particles present in the record, with diameters up to 1·7 micron. It is not quite clear what the path of the wind was before reaching Holme; it may have come from the furnaces of the North-East Coast of England, but it may, on the other hand, have been the haze of the previous N.E. wind drifting back

again, though that is not very likely. The deposit of August 27 may have come from Hunstanton, as the wind was from that direction.

On August 28, at 9 A.M., after calm and a little rain, the wind came from N. with clear air, but at 15 h. a slight haze came with a veer to the N.E. in the surface wind. The clouds came from the south throughout the day.

On August 30 there was very clear air with a moderate wind from N.N.W. and on this occasion drops of liquid were found with the deposit which, after being mounted a month, developed into crystals, presumably of common salt. But this was the only one of the records which gave this result, and any inference from it is hazardous; the liquid drops seemed to be separate from the dust particles and may have been separately suspended in the air.

On August 31 there was haze with westerly wind which disappeared with a change to N.E. and rain; the haze followed a cold, clear night and was dense in the early morning with westerly wind; but it was shallow, because the tops of the trees were more visible than the bottoms. The haze got lighter by 1 P.M., with the wind still west. The wind was round to N.E. by 4 P.M. and calm with a few drops of rain at 8 P.M.: by then the haze had gone. The indications are too vague for any conjecture as to the origin of the impurities which formed the haze in this case.

It is probable that regular observations, at any place, with different winds, would give some indication of the most likely source of the dust; for example, the author has found that when the wind blows from the direction of London, samples of air taken at Cheam, in Surrey, invariably contain large numbers of suspended particles of the same size and general appearance as those forming the London haze. When the wind blows from the opposite direction it contains few such particles. The smoke produced in the manufacturing districts of England probably drifts over hundred of miles, under suitable conditions, producing an impure air in the depths of the country. This is a point of some importance, as it is usually assumed that by going a few miles outside the city pure air can be obtained, which is very far from being the case, under present conditions.

During a recent visit to Exmouth, the author noticed that the whole country was obscured by a well-marked haze, which produced a red sunset, and doubtless had its origin from the smoke of the manufacturing districts of the Midlands, as there had been a light wind from the north for some time. Unfortunately samples could not be obtained, but from the appearance of the haze there is little doubt that it was composed of solid particles.

Table II.—Number of Dust Particles in the Air according to Various
Observers.

Observer.	Method of collection of dust and counting.	Place of investigation.	Number of particles per cubic centimetre.	Reference.
John Aitken	Aitken's dust counter*	Argyllshire London	300/3000 48,000 to 150,000	'Trans. Roy. Soc. Edin.,' vols. 30–36
B. C. and M. C. Whipple	Agitation with water in Palmer's apparatus and counting in a cell under microscope†	Boston, U.S.A., ground level 58th floor	4·2 <1	'Amer. Jour. Public Health,' 1918, 3, 1139
Dr. Penteado Bill	Electrostatic precipitation	—	From 22 to <1	'Jour. Ind. Hygiene,' vol. 1, No. 7, 1919

* It is not certain what is counted in the apparatus. Nuclei other than dust, such as electrons, are included.

† When in water, as shown in present paper, the smaller particles are lost. As shown by Katz, Fieldner and Longfellow, 'Jour. Ind. Hygiene,' vol. 11, No. 5, the Palmer apparatus is about 20–80 per cent. efficient in removing dust from air.

A Table (Table II) is given here, showing the dust counts as obtained by other observers, using different methods. The extraordinary variation in the number of particles as given is remarkable, and points towards some uncertainty in the methods adopted.

The Structure of the Band Spectrum of Helium.

By W. E. Curtis, A.R.C.S., B.Sc., Reader in Physics in the University of London, King's College.

[Plate 1.]

Introductory.

The band spectrum of helium was first described by Goldstein[*] and by the present writer[†] in 1913. The accounts given of the spectrum, and of the conditions favouring its production, were closely similar, but in neither case was any analysis of its structure attempted. In view of the somewhat complex character of the spectrum in certain regions, it appeared advisable for this purpose to secure a series of high dispersion plates, while the apparently abnormal nature of many of the bands provided a further incentive to their study on the largest scale possible. Accordingly, a number of exposures were made in the first, second, and third orders of the 10-foot concave grating of the Royal College of Science, London. Of these plates some seven or eight were suitable for measurement, only one of which, however, was in the third order. The outbreak of the War prevented the completion of the series of exposures contemplated, but sufficient material was accumulated to permit of a reasonably complete investigation of the spectrum between the limits 6480 — 3350 Å. A preliminary examination of these plates was made by Prof. Fowler[‡] in 1914 (the author being on military service), and resulted in the detection of two series of double-headed bands presenting certain unusual features, of which the most striking was their distribution according to a line-series law. Nicholson,[§] using Fowler's measures, calculated new formulæ for these series, and concluded that they were analogous to principal series in line spectra. No other work relating to the structure of the spectrum seems to have been published.

Apart from the doublet bands studied by Fowler, the most prominent features of the spectrum are a red band near λ 6400 and a green band near λ 5730, both of which appear, under moderately high dispersion, to have a quite abnormal structure. As these two bands seemed to promise more immediately interesting results than the remainder, they were the first to be

[*] 'Verh. Deutsch. Phys. Gesell.,' vol. 15, p. 402 (1913).
[†] 'Roy. Soc. Proc.,' A, vol. 89, p. 146 (1913).
[‡] 'Roy. Soc. Proc.,' A, vol. 91, p. 208 (1915).
[§] 'Roy. Soc. Proc.,' A, vol. 91, p. 432 (1915).

studied, a band in the blue (near λ 4550), which appeared to be related to λ 6400, being subsequently included in the investigation. The results obtained in connection with these three bands form the subject of the present com- munication. The structure of the remainder of the spectrum, including Fowler's doublet bands, will be discussed, it is hoped, in a future paper.

Detailed analysis of the three bands in question soon confirmed the opinion that their structure was strikingly different from that of "ordinary" bands, as may readily be seen by reference to the plate. In each case there is one series (two in λ 5730) which proceeds to a head, and several others which do not. The latter usually occur in pairs situated on either side of the former, and exact measurement and calculation suggest that each pair may be regarded as forming one series, of which several lines (usually two) near the middle are missing.

So far as was known these anomalous features had no counterpart in any other spectrum, with the possible exception of the ammonia band at λ 3360. Fowler's[*] photographs and diagrams of this band show some striking resemblances to the helium bands under consideration, but the analysis of the former is more difficult, partly because it is composed of triplets, and partly because, by reason of its situation in the ultra-violet, the wave-numbers are very sensitive to errors in wave-lengths. But it is thought that some at least of the results here obtained may assist in the interpretation of the structure of the ammonia band.

The main characteristics outlined above had been established early in 1919, and as there seemed little promise of further progress with the somewhat limited data available, experimental work[†] was undertaken, with a view to obtaining fresh information relating to the structure of the spectrum as a whole. That is to say, it was hoped to decompose the spectrum into families of bands and then to investigate the arrangement of the members of each family. By varying the conditions of pressure and electrical excitation distinct evidence of changes of relative intensity, and even of the production of new bands, was obtained, but before work along these lines had progressed very far some recent theoretical work on band spectra came to the author's notice, and was found to have an immediate bearing on the present problem. It appeared that this theory was not only capable of accounting for the apparent anomalies of structure and of exhibiting the manner in which these and ordinary bands are related, but also yielded information of a quantitative character concerning the structure of the molecules and atoms which emit the

radiation. An excellent résumé of the work in question will be found in Sommerfeld's 'Atombau und Spectrallinien' (Vieweg, Braunschweig, 1921), pp. 550–566; a short account is also given in a recently published monograph on 'Series Spectra,' by N. R. Campbell (Camb. Univ. Press, 1921). As the treatment here adopted differs slightly from Sommerfeld's, it has been thought advisable, in order to render what follows intelligible, to give a brief outline of the theory before discussing its application to the helium bands.

The Quantum Theory of Band Spectra.

In conformity with a great deal of experimental evidence the theory attributes band spectra to molecules; these are treated (in the first instance) as rigid bodies possessing internal and rotational energy, either or both of which may vary, giving rise to emission or absorption of energy in the form of radiation. The former case is alone considered here. The fundamental assumptions are those employed by Bohr in his theory of line series, and now generally recognised as of wide validity, viz.:—

(1) The emission of a frequency ν is due to a decrease $h\nu$ in the energy of the radiating system.

(2) If the system is in rotation and is not emitting radiation its angular momentum must be an integral multiple of $h/2\pi$. There is thus a limited number of possible angular velocities, just as in Bohr's model of the hydrogen atom there is a limited number of stationary electron orbits.

Let 1 and ω respectively represent the moment of inertia (about the axis of rotation) and the angular velocity of the molecule. Then if the rotation quantum number m changes to m' ($m' < m$), the energy radiated

$$= h\nu = \tfrac{1}{2}I\omega^2 - \tfrac{1}{2}I\omega'^2 \text{ by (1).}$$

But
$$I\omega = \frac{mh}{2\pi} \text{ by (2).}$$

Thus
$$h\nu = \frac{1}{2I}\left\{\left(\frac{mh}{2\pi}\right)^2 - \left(\frac{m'h}{2\pi}\right)^2\right\} = \frac{h^2}{8\pi^2I}(m^2 - m'^2).$$

According to the selection principle of Rubinowicz m cannot change by more than one unit at a time, so that we shall have

$$\nu = \frac{h}{8\pi^2I}(2m-1).$$

This represents a series of equally spaced lines, and from existing data in connection with molecular moments of inertia (of the order of 10^{-40} for the lighter molecules) we conclude that they must lie in the far infra-red, round about 30μ. In spite of the great difficulties attending work in this region a certain amount of evidence confirmatory of the theory has been obtained (e.g.,

for water-vapour absorption by Rubens and by v. Bahr), but accurate measurements are not possible at present. If, however, we suppose, as Schwarzschild suggested, that a change in the configuration of the molecule involving a decrease $h\nu_0$ in the internal energy may occcur simultaneously with the change in angular momentum, the resultant frequency radiated may be very much greater than those characterising the pure rotation spectrum, so that it may be brought into the region where spectroscopic investigation is more easily and accurately conducted than in the far infra-red.

The configuration change referred to may primarily concern the positions of the electrons or of the atoms within the molecule. In the former case the consequent alterations in the electrical forces are bound to affect the distance apart of the atoms, so that in both cases the final moment of inertia will differ in general from the initial. Thus, if the moment of inertia takes the value I' after the configuration change, we shall have

$$h\nu = h\nu_0 + \frac{h^2 m^2}{8\pi^2 I} - \frac{h^2 (m-1)^2}{8\pi^2 I'} \qquad [m \to (m-1)$$

whence
$$\nu = \nu_0 - \frac{h}{8\pi^2 I'} + \frac{h}{4\pi^2 I'} \cdot m + \frac{h}{8\pi^2}\left(\frac{1}{I} - \frac{1}{I'}\right) m^2,$$

or writing c_0' for $\dfrac{h}{8\pi^2 I'}$ and c_2 for $\dfrac{h}{8\pi^2}\left(\dfrac{1}{I} - \dfrac{1}{I'}\right)$,

$$\nu = \nu_0 - c_0' + 2c_0' m + c_2 m^2.$$

Two other cases are also possible. First, the angular momentum may remain unaltered during the change $h\nu_0$. The frequency emitted will, however, be modified in consequence of the change in the moment of inertia, so that

$$\nu = \nu_0 + c_2 m^2 \qquad [m \to m.$$

Finally,[*] the rotation quantum number may increase from $(m-1)$ to m, giving

$$\nu = \nu_0 + c_0 - 2c_0 m + c_2 m^2 \qquad [(m-1) \to m$$

where c_0 denotes $\dfrac{h}{8\pi^2 I}$.

Evidently
$$c_0 - c_0' = c_2.$$

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[*] Here the treatment departs slightly from that of Sommerfeld, who considers the change $m \to (m+1)$, and thus obtains an expression identical with the first, except that the coefficient of m is negative (*i.e.*, $-2c_0'$), so that both series are represented by one formula in which m takes both positive and negative values. The method adopted in the text has the advantage of making the numbering symmetrical, *i.e.*, lines associated with the same two quantum states are denoted by the same value of m in the formulæ, whereas by Sommerfeld's treatment they are denoted by $+m$ and $-(m+1)$. Further,

Adopting the notation of Heurlinger we shall write $R(m)$, $Q(m)$ and $P(m)$ respectively, for the general term of each of these series. Thus for the

$$\text{positive branch } R(m) = \nu_0 - c_0' + 2c_0'm + c_2m^2,$$

$$\text{null (zero) } \quad \text{,, } \quad Q(m) = \nu_0 + c_2m^2,$$

$$\text{negative } \quad \text{,, } \quad P(m) = \nu_0 + c_0 - 2c_0m + c_2m^2.$$

Only positive integral values are to be given to m.

Graphically interpreted these equations represent a system of similar parabolas having their axes parallel to the ν axis. The vertex of the Q parabola is on the ν axis, and the vertices of the P and R parabolas are nearly equidistant from it and on opposite sides. The latter curves are, in fact, reflections of one another in the line $m = \frac{1}{2}$.

A typical set of series is represented in fig. 1; they have been calculated for the case when $c_0 = 15\cdot5$ $(cm.^{-1})$, $c_0' = 14\cdot5$ and accordingly $c_2 = +1$, values which are not far removed from those found in connection with the helium bands. The lower part of the diagram illustrates the actual appearance of the bands on a uniform scale of wave-numbers, except that to avoid confusion the Q series has been plotted separately from the other two, and the two series proceeding from the P head have also been separated.

If c_2 had been negative (corresponding to $I' > I$) a similar set of series would have been obtained, but degraded in the opposite direction, *i.e.*, to the less refrangible side. Further, the R series and not the P series would then have proceeded to a head.

On this theory the head of a band assumes only a secondary importance in comparison with the frequency ν_0; it is merely a region where the lines happen to be crowded together, and its location is of no primary significance in connection with the structure of the band. For example, in seeking relationships between different bands, it is to be expected that the laws expressing these will take their simplest form when they are formulated in terms of the respective values of ν_0, instead of the frequencies of the heads. For series of the Q type the distinction is unnecessary, since the head is at

the former method was thought to be more convenient for testing the applicability of the theory, since the empirical representation of both series in a single formula would have necessitated the employment of higher powers of m than would be required in the separate treatment of the two series, so increasing considerably the labour of computation. But the numbering adopted by Sommerfeld has been generally used, and for that reason is possibly to be preferred.
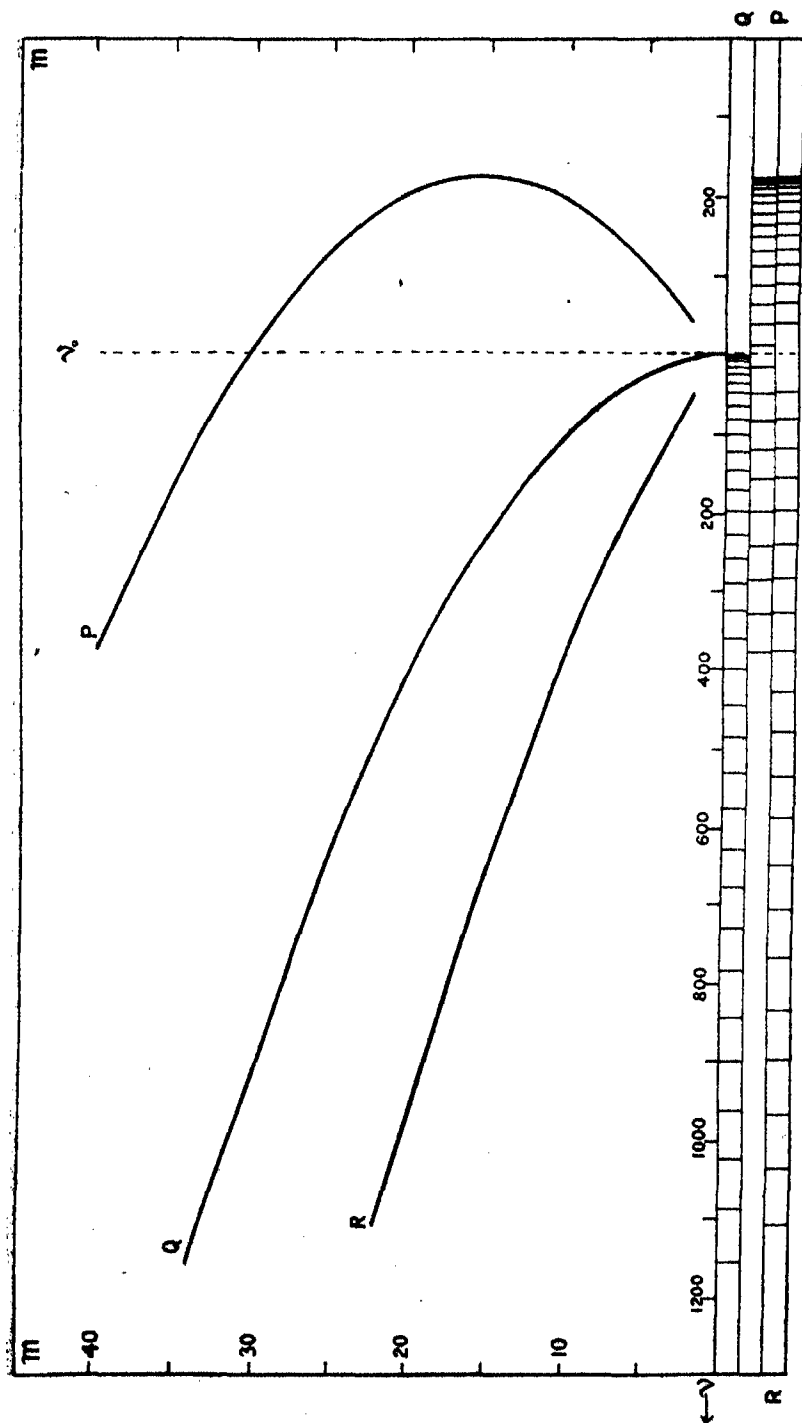
Fig. 1.—Theoretical group of band series.

$R(m) = \nu_0 - c_0' + 2c_0'm + c_2m^2$; $Q(m) = \nu_0 + c_2m^2$; $P(m) = \nu_0 + c_0 - 2c_0'm + c_2m^2$; $c_0 = 15\cdot5$, $c_0' = 14\cdot5$, $c_2 = c_0 - c_0' = 1\cdot0$ cm.$^{-1}$.

ν_0, but the head of the P or R series (whichever may happen to possess one) may be shown to be given by

$$m = \frac{c_0}{c_2} \text{ (P series) } \quad \text{or} \quad -\frac{c_0'}{c_2} \text{ (R series)}$$

and

$$\nu = \nu_0 - \frac{c_0 c_0'}{c_2},$$

i.e.,

$$\nu = \nu_0 + \frac{h}{8\pi^2(I - I')}.$$

It may be noted that the term "head" as here employed refers to the vertex of the parabola, which does not necessarily correspond with an actual line, and indeed will in general not do so.

Many of the characteristics of band structure outlined above were recognised by Heurlinger[*] independently of the theory, and he and others have subsequently shown that the structure of many typical bands (e.g., nitrogen and "cyanogen") may be interpreted by its aid, provided certain modifications are made in some cases. For example, the Q series is frequently absent, and there may be six or twelve series in all, instead of three, but as these complications do not occur in helium they need not be considered here. One feature which is common to all the bands studied must, however, be mentioned, namely, the gap (indicated in the figure) which occurs between the P and R series. The fundamental frequency ν_0 is invariably absent from the spectrum, and often one or more of the adjacent lines are also suppressed. The absence of the former has been attributed to the non-existence of molecules having no rotational energy, which would obviously be the only ones capable of giving rise to it, and this view is not without some support on other grounds (e.g., investigations on the specific heat of hydrogen at low temperatures). This explanation would at the same time account for the absence of the adjacent lines P(1) and R(1), for these are due to the transitions $0 \to 1$ and $1 \to 0$. These lines are, in fact, absent from the helium bands so far studied, and have therefore been omitted from fig. 1. But it appears that the above explanation fails in the case of the "cyanogen" band at λ 4216, where ν_0 is absent, but the pair of lines given by $m = 1$ actually occurs. We may perhaps, in this and similar cases, infer that the non-rotating molecule is capable of existing, but incapable of emitting its characteristic frequency ν_0 without a simultaneous change in its angular momentum. In this connection Lenz[†] has proposed to introduce a second quantum number n, which relates to the angular momentum about

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[*] 'Untersuchungen über die Structur der Bandenspektra,' Diss. Lund., 1918.
[†] 'Verh. d. Phys. Ges.,' vol. 31, p. 632 (1919).

an axis perpendicular to that associated with m. For example, in the Bohr-Debye model of the hydrogen molecule n would refer to rotation about the axis of figure (the line joining the atoms) and m to that about a perpendicular axis through the centre of gravity of the atoms. He thus obtains a formula

$$\nu = \nu_0 + c_1 (m + n) + c_2 (m + n)^2$$

in which m can take all possible integral values, but n can never be less than a certain minimum value dependent upon the structure of the molecule (*e.g.*, if there are two electrons revolving in an orbit perpendicular to the axis of figure, n could never be less than 2). Evidently in such a case the first n_0 lines will be missing from each of the P and R series, n_0 denoting the above-mentioned minimum value of n.

The actual appearance of the bands originating in this manner will be determined not only by the location of the lines but also by their intensities. These depend upon the way in which the various possible angular velocities are distributed amongst the molecules. Theory indicates some general features of this distribution which appear to be in accordance with observation, although precise measurements of intensities have not been made. Thus, for example, as m increases the intensities increase pretty rapidly, reach a maximum and then decline much more slowly. Also, the greater the moment of inertia of the molecule the greater will be the proportion of molecules possessing large angular momenta; in other words the number of lines of observable intensity will be greater. Increase of temperature will produce a similar effect.

In conclusion, the special characteristics which might be anticipated for the helium bands (as compared with those due to heavier elements and compounds) may be indicated. Whatever the constitution of the molecule responsible for their production, it is likely that its moment of inertia will be relatively small, considerably smaller than, say, that of the nitrogen molecule, so that the frequency intervals between the lines in the neighbourhood of ν_0 should be relatively large, since these are (approximately) inversely proportional to I. Further, the series will comprise comparatively few members, and may in the case of the P and R branches fade into invisibility before the head is reached, so causing a conspicuous difference in appearance from that of an "ordinary" band series, in which the head is the most prominent feature. These expectations are found to be realised in the case of the three bands under examination, and their anomalous character in these respects is thus seen to be only apparent.

The Band λ 6400.

The general appearance of this band will be seen from the Plate, and the manner in which it has been analysed is shown in fig. 2, which is a graphical representation on a scale of wave-numbers, intensities being also indicated.
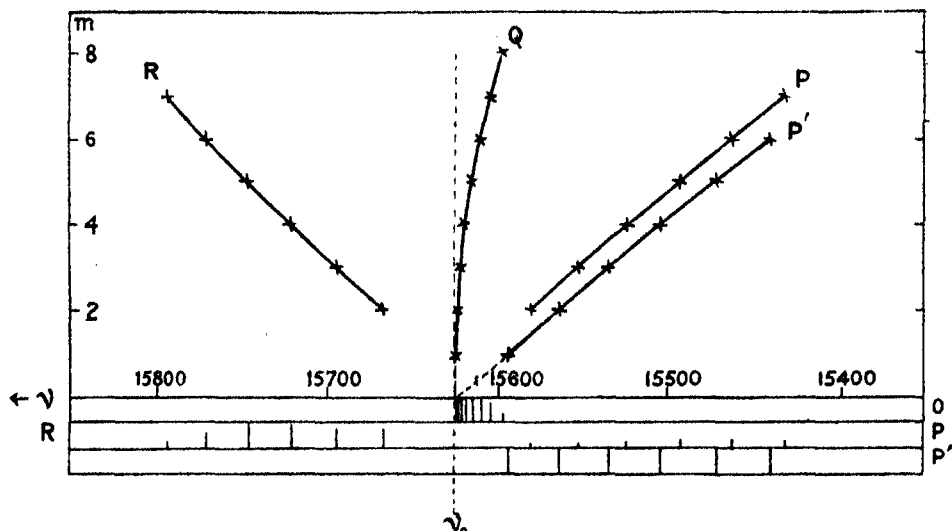
Fig. 2.—Helium band at λ 6400.

Full details of the band are collected in Table I, which gives the estimated intensities, wave-lengths (I.A., air) and wave-numbers (*vacuo*) of all the lines of the four series recognised. These were obtained from a first-order grating plate which had an exposure of about 6 hours on the bulb of a Plücker tube containing helium at a few millimetres pressure (estimated) and excited by an oscillatory discharge of moderate intensity. The absolute wave-lengths are not very reliable, on account of the liability to temperature shift during an exposure of this length, and may be in error by 0·1 Å. or so (as estimated from previous experience of the instrument). But for the present purpose such a shift, so long as it is reasonably small, is of little importance. Relatively to each other the wave-lengths should be accurate within the limits of measurement, which is estimated (by comparison of different sets of measures) at about 0·02 Å., corresponding to 0·05 unit in the wave-number. The estimates of intensity were made at the first measurement (in 1914) before the allocation into series, and were not subsequently revised (only checked). The wave-lengths of Burns[*] were used for the iron arc comparison lines, and the Bureau of Standards Tables[†] for the reductions to vacuum.

[*] 'Lick. Obs. Bull.,' No. 247, 1913.
[†] 'Scientific Paper,' No. 327, 1918.

Table I.—Details of the Band λ 6400.

	R series.				Q series.		
m.	Int.	λ (air).	ν (vac.).		Int.	λ (air).	ν (vac.).
1					10	6398 ·74	15623 ·77†
2	8	6381 ·21	15666 ·68		10	99 ·26	22 ·50
8	8	70 ·02	94 ·21		10	6400 ·02	20 ·64
4	9	59 ·22	15720 ·88		10	01 ·19	17 ·79
5	10	48 ·89	46 ·44		10,	02 ·73	14 ·04
6	6	39 ·06	70 ·86		10	04 ·62	09 ·43
7	8	29 ·80	93 ·93		8	06 ·85	03 ·09
8					3†	09 ·48	15597 ·58

	P series.				P′ series.		
m.	Int.	λ (air).	ν (vac.).		Int.	λ (air).	ν (vac.).
1					10	6410 ·79	15594 ·89
2	1	6415 ·92	15581 ·92		10	23 ·10	64 ·51
8	1	28 ·11	52 ·38		10	35 ·68	34 ·09
4	2	40 ·38	22 ·75		10	48 ·49	03 ·23
5	2	52 ·76	15492 ·96		10	61 ·47	15472 ·08
6	2	65 ·32	62 ·89		10	74 ·59	40 ·73*
7	2	78 ·12	32 ·31*				

* The next members of these series are just off the edge of the plates available for accurate wave-length determinations, but several more appear on plates taken with other instruments of less dispersion.

† This line might alternatively be regarded as the first of the P′ series, but as the corresponding lines of the 5730 and 4546 bands are certainly Q (1). in each case this has been designated Q (1) also.

Formulæ were next calculated for the four series. Examination of the second differences showed that the wave-numbers could not be represented by a formula of the type $\nu = a + bm + cm^2$, but that at least one additional term of higher order would be required. A third order term was introduced, and was found to be sufficient for a satisfactory representation in all cases. The coefficients were calculated by the method of least squares, and are exhibited in Table II, which also gives the corresponding residuals.

The similarity between the disposition of the series designated P, Q and R and that of the theoretical family illustrated in fig. 1 is apparent from the figure, and we see at once that the unusual appearance of this band is chiefly due to the small number of lines developed, so that the head which would be expected in the R series cannot be observed. The extreme faintness of the P series and the presence of a very strong additional series (P′) are other circumstances which help to disguise the true character of this band, but the

calculations which follow leave no doubt that the structure is in the main identical with that required by the theory.

<div align="center">Table II.</div>

Coefficients in Formulæ for λ 6400 Series.   Residuals.

| Series. | m^0. | m. | m^2. | m^3. | (O − C) × 100. | | | | | | | |
					1.	2.	3.	4.	5.	6.	7.	8.
R	15609·61	+ 29 ·045	− 0 ·2015	− 0 ·02667		0	− 1	+ 2	− 2	− 1	+ 2	
Q	15624·08	+ 0 ·066	− 0 ·4004	− 0 ·00273	+ 3	− 9	+ 4	+ 3	− 2	− 4	0	0
P	15641 ·38	− 30 ·005	+ 0 ·1805	− 0 ·02300		+ 1	+ 2	− 3	− 2	0	+ 1	
P′	15623 ·73	− 28 ·951	− 0 ·3662	+ 0 ·01798	− 5	0	+ 2	0	0	0		

Theoretical formulæ :—

$$R\ (m) = \nu_0 - c_0' + 2c_0'm + c_2 m^2.$$
$$Q\ (m) = \nu_0 + c_2 m^2.$$
$$P\ (m) = \nu_0 + c_0 - 2c_0 m + c_2 m^2.$$
$$P'(m)\ \text{(see p. 50)}.$$

From Table II it will be seen that third power terms appear in the formulæ; they are in fact necessary for the representation of the series, and must correspond to some factor not taken into account in the theory as presented above, a factor which we shall for convenience refer to as the "perturbation" without enquiring at present into its nature. There may of course be more than one such factor, but their total effect on ν may be represented by a function $a + bm + cm^2 + dm^3$ which when added to the simple second-order theoretical formula gives the empirical formula actually obtained. The coefficient of m^3 in the latter is equal to d, but the values of a, b and c cannot be determined, and therefore the relations which should theoretically exist between the coefficients of m^0, m and m^2 are not likely to be exactly satisfied, so that a complete verification of the theory is not to be expected.

Proceeding now to compare coefficients of the theoretical and experimental formulæ, we obtain,

(1)   From P, $\nu_0 + c_0 = 15641 \cdot 38$, $c_0 = 15 \cdot 00$,   ∴ $\nu_0 = 15626 \cdot 38$,

     „   R, $\nu_0 - c_0' = 15609 \cdot 61$, $c_0' = 14 \cdot 52$,   ∴ $\nu_0 = 15624 \cdot 13$.

The difference between the two values of ν_0 is presumably due to the coefficients a and b of the function expressing the perturbation, and is small enough to justify the application of the theory to these series, particularly as the value of ν_0 derived from the Q series, i.e., 15624·08, is also in agreement.

(2) The second theoretical relation between the coefficients of the three formulæ is that c_2, the coefficient of m^2, should be the same for all, and equal $(c_0 - c_0')$. To test this, we have—

$$\text{from P and R,} \quad c_0 - c_0' = +0\cdot48,$$
$$\text{,, R} \qquad\qquad c_2 = -0\cdot20,$$
$$\text{,, Q} \qquad\qquad c_2 = -0\cdot40,$$
$$\text{,, P} \qquad\qquad c_2 = +0\cdot18.$$

The expected relation is not established, but the terms in question are so small that the perturbation is probably relatively important in this case. The disagreement indicates that the values obtained above for c_0 and c_0' may not be very reliable, within perhaps 3 per cent. or so.

Taking them for what they are worth, however, the corresponding moments of inertia may be calculated, with the following results :—

$$\text{Initial value I} = \frac{h}{8\pi^2 c_0} = 1\cdot84 \times 10^{-40} \text{ grm.-cm.}^2$$

$$\text{Final value I}' = \frac{h}{8\pi^2 c_0'} = 1\cdot90 \times 10^{-40} \text{ grm.-cm.}^2$$

where h has been taken as $6\cdot54 \times 10^{-27}$ erg-sec., and c_0, c_0' are expressed as frequencies (3×10^{10} times the previous values).

The Q series, it may be noted, conforms closely to the theoretical requirements in that the coefficients of m and m^3 are both very small. It is, therefore, capable of approximate representation by a parabola with vertex at $m = 0$, $\nu = \nu_0$, while $m = 1$ gives the first observed line. The absence of $Q(0)$ is to be expected in view of the absence of $P(1)$ and $R(1)$, and supports the conclusion that the non-rotating molecule does not occur. The smallness of the perturbation in this case also allows the numeration to be determined without ambiguity, and suggests that the value of ν_0 deduced, viz., 15624·1, is probably the best that can be derived for these series.

The additional series P' has no counterpart in the theoretical group of series, but is nevertheless intimately related to the three already dealt with. The nature of the relationship is readily seen from the figure, and may be expressed as follows :—

(1) P' is approximately parallel to P, *i.e.*, the coefficients of m are of the same order of magnitude in both cases.

(2) P' extrapolates to ν_0 derived from the Q series, *i.e.*, $P'(0) = Q(0)$ within the limits of experimental error. As a matter of fact, the line $Q(1)$, 15623·77, would fit equally well in the P' series as $P'(0)$, but the former identification is here preferred, because it agrees with that adopted for the

other bands studied, where the corresponding lines are certainly Q(1) and not P' (0).

It may be noted that the numeration of this series cannot be definitely settled at present, since the mechanism of its production is not understood; that employed must therefore be regarded as provisional.

The formula representing this series will be seen to be of the form

$$P'(m) = \nu_0 - 2c'm + c_2'm^2,$$

where ν_0 is identical with that characteristic of the P, Q, and R series, and c', c_2' are not very different in magnitude from the corresponding coefficients of the normal family. Further discussion of this series may be postponed until the other two bands have been considered.

The Band λ 4546.

The details of this band are given in Table III. Again, only one plate suitable for measurement was available, and comparison of several independent sets of measures shows that the wave-numbers are probably less

Table III.—Details of the Band λ 4546.

	R series.				Q series.	
m.	Int.	λ (air).	ν (vac.).	Int.	λ (air).	ν (vac.).
1				3	4545·80	21992·21
2	3	4537·14	22034·15	4	46·21	90·20
3	3	31·71	60·54	6	46·98	86·75
4	3	26·66	85·15	6	47·91	82·00
5	3	21·92	22106·84	6	49·16	75·90
6	3	17·62	29·38	5	50·81	67·96
7	1	13·66	48·79	4	52·72	58·80
8				3	55·04	47·56

	P series.				P' series.	
m.	Int.	λ (air).	ν (vac.).	Int.	λ (air).	ν (vac.).
1				4	4551·80	21968·20
2				6	58·20	32·85
3				6	64·62	00·56
4	0	4564·27	21903·2 ?	6	71·69	21867·68
5	1−	70·48	21873·42	6	78·75	33·92
6	1	76·98	42·36	6	85·97	21799·55
7	1	83·72	10·25	3	93·45	64·04
8	1	90·68	21777·19	1	4601·12	27·79
9	1	97·88	48·10			

The line P (4), marked P, was too weak to measure satisfactorily, and the tabulated wave-number may be in error by 0·3 or so.

accurate than before, partly owing to the larger value of $d\nu/d\lambda$ in this region, and partly also on account of the slightly winged character of the lines (attributed to temperature shift during the 7 hours' exposure). It is believed that the relative errors in wave-number will seldom exceed 0·15 unit however. The P series was so faint that it could not be measured on the iron arc overlap, and the previously determined P′ lines were therefore utilised as standards. This procedure necessarily increased the probable error somewhat. A few lines (all faint) evidently not connected with the series have not been recorded.

Table IV exhibits the formulæ and residuals in the same manner as before. The accuracy of the wave-numbers did not justify the calculation of third power terms ; in fact, quadratic formulæ sufficed for the representation of all the series except Q, where a further term would have been required to include the eighth member.

<div align="center">Table IV.</div>

Coefficients in Formulæ for
λ 4546 Series.   Residuals.

Series.	m^0.	m.	m^2.	(O−C) × 100.								
				1.	2.	3.	4.	5.	6.	7.	8.	9.
R	21975 ·99	+ 30 ·818	−0 ·8761		+ 2	− 2	− 11	+ 14	0	− 2		
Q	21992 ·64	+ 0 ·244	−0 ·7250	+ 6	− 3	− 9	− 2	+ 17	− 4	− 2	(−63)	
P	22013 ·80	− 25 ·571	−0 ·5007				(−30)	0	+ 2	− 2	0	0
P′	21993 ·35	− 29 ·640	−0 ·4449	− 7	+ 4	+ 13	− 4	− 11	+ 5	− 3	+ 3	

Residuals in brackets refer to lines not used in obtaining formulæ, e.g., Q (8) is unreliable, as it is a blend with a stronger line.

<div align="center">

From P, $\nu_0 + c_0 = 22013 ·80$, $c_0 = 12 ·79$, ∴ $\nu_0 = 22001 ·0$.
  „ R, $\nu_0 - c_0' = 21975 ·99$, $c_0' = 15 ·41$, ∴ $\nu_0 = 21991 ·4$.
  „ Q, $\nu_0 \quad = 21992 ·64$.

</div>

The similarity of this band to λ 6400 is apparent from fig. 3 ; both consist of a " normal " family of P, Q, and R series, the first being much weaker than the other two, together with a strong additional series (P′), running roughly parallel to the P series and commencing at the head of the Q series. Both families are degraded toward the less refrangible side, corresponding on the theory to a decrease in the moment of inertia of the molecule as a result of the configuration change.

It will be seen from Table IV that while the two values of ν_0 from Q and R agree very well, that from P is discordant by about 10 units. It should be noted, however, that this series was not completely observed : P (4) was too

weak to measure reliably, $P(3)$ would fall under $P'(2)$, and $P(2)$ was not present. The value of ν_0 in the case of this series is therefore derived from a long extrapolation, namely, from $P(5)$ to $P(0)$, and is entitled to but little weight. A displacement of the series may possibly exist, but cannot be certainly established from the data available. As the coefficient of m is affected by a similar uncertainty, a better value of c_0 is probably obtainable from the well determined R series by utilising the theoretical relation $c_0 - c_0' = c_2$. We have $c_0' = 15\cdot4$, $c_2 = -0\cdot8$ (mean of Q and R values) whence $c_0 = 14\cdot6$. These values correspond to initial and final moments of inertia of $1\cdot89 \times 10^{-40}$ and $1\cdot79 \times 10^{-40}$ respectively. In view of the method by which these figures have been obtained, it would be inadvisable to attach
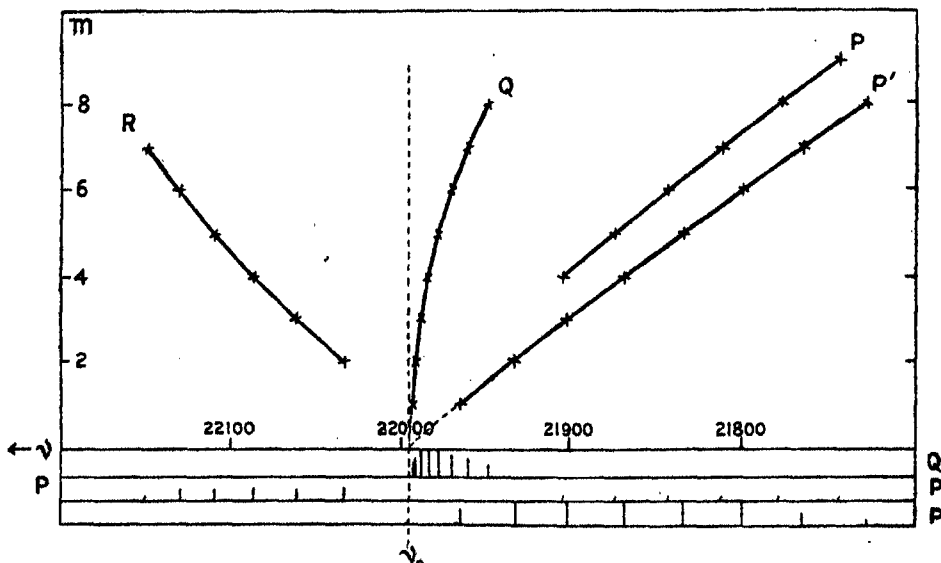
Fig. 3.—Helium band at λ 4546.

too much weight to them, but it is probably justifiable to conclude that the average moment of inertia is of the order of $1\cdot8$ to $1\cdot9 \times 10^{-40}$. In the case of the band λ 6400 the average moment of inertia was found to be $1\cdot87 \times 10^{-40}$. This agreement lends further support to the view that these two bands are closely related in some way.

If the two bands were associated in the manner characteristic of line series, as found by Fowler (loc. cit.) for other bands in this spectrum, we should expect to find the next member near $\nu = 24820$, and it should be of observable intensity. On the plates available this region is a confused mass of lines in which no regularities have been established as yet, and it is possible that the hypothetical band may have escaped detection. At all

events its absence cannot be proved. The next member might be expected at about 26320, with, of course, a rather large probable error. There is a weak single head at 26466, which is degraded towards the red and might from its appearance be associated with $\lambda\lambda$ 6400 and 4546, but on the high dispersion plates it is too weak to measure satisfactorily. It is hoped that further experimental work may throw some light on this question. Meanwhile, it may be remarked that there is just a possibility that the band at 26466 may be the third member of the series instead of the fourth. If this were the case the series law would be rather a curious one, namely, the squares of the frequencies would be approximately as $1 : 2 : 3$, *i.e.*, the wave-numbers would be in the ratio $1 : \sqrt{2} : \sqrt{3}$. The exact figures are as follows :—

$$\nu_1 = 15624 = 1\cdot562 \times 10^4,$$

$$\nu_2 = 21992, \qquad \frac{\nu_2}{\sqrt{2}} = 1\cdot555 \times 10^4,$$

$$\nu_3 = 26466, \qquad \frac{\nu_3}{\sqrt{3}} = 1\cdot528 \times 10^4.$$

In this case the next member would fall at about $\nu = 30,000$, which is just outside the region covered by the plates.

The Band λ 5730.

This band is visually the most prominent feature of the spectrum, and differs from the remainder in being degraded towards the more refrangible side. It is rather more complex than the two bands already described, but the results established for these have been of great assistance in elucidating its structure. Again the measurements were all made on one plate (first order, 10 hours' exposure); the wave-lengths are probably reliable to about 0·02A, and the wave-numbers to 0·06 cm.$^{-1}$, in both cases relatively to each other. These particulars, with intensities and series allocation will be found in Table V, which also includes all lines which appear on the plate but have not been allocated to series. These cannot be traced to any impurity or accident (*e.g.*, ghosts, superposed orders), and some at least of them may prove to be associated with the band.

Six series have been recognised in this band, and the coefficients of the formulæ calculated for them are shown in Table VI. In several cases a fourth power term appeared to be required in order to secure a satisfactory representation, suggesting a rather larger perturbation than in the previous cases, although the slightly greater extension of these series is no doubt partly responsible.

Table V.—Details of the Band λ 5730.

Int.	λ (air).	ν (vac.).	Series.	Int.	λ (air).	ν (vac.)	Series.
1−	5645·87	17707·28	R (8)	8	5748·60	17390·74	
1−	50·93	17691·86	R' (8)	1	49·15	89·08	
1	58·44	67·81	R (7)	2	50·17	86·00	
1	60·12	62·58	R' (7)	1+	51·10	83·27	
2	70·07	31·59	R' (6)	5	51·69	81·38	P' (2)
2	71·18	28·28	R (6)	1	52·09	80·19	
8	80·50	17599·20	R' (5)	1	52·84	77·98	
4	83·58	89·67	R (5)	1+	53·54	75·78	
5	91·27	65·92	R' (4)	7	56·21	67·74	P (3)
6	95·64	52·44	R (4)	9	59·82	56·86	P' (3)
1−	97·42	47·08		9	64·45	42·91	P (4)
6+	5702·18	82·44	R' (3)	9	67·10	34·94	P' (4)
1−	04·90	24·02		1	69·55	27·58	
7	07·15	17·08	R (3)	9	72·33	19·23	P (5)
1−	08·14	14·06		10	73·59	15·47	P' (5)
7	12·91	17499·38	R' (2)	1+	77·26	04·48	
1	14·58	94·15		8	79·29	17298·87	P_1' (6)
2	16·23	89·10	Q_1 (7)	8	80·09	96·00	P (6)
7	18·10	83·47	R (2)	5	84·38	88·16	P' (7)
1−	18·77	81·48		1	85·31	80·37	
8	19·99	77·70	Q_1 (6)	3	86·95	75·57	
2	21·18	74·06		5	87·79	72·98	P (7)
2	21·98	71·64		8	89·00	69·35	P' (8)
10	23·39	67·30	{ Q_1 (5) / R' (1) ?	2−	98·36	56·28	P' (9)
8	24·86	62·85	Q_2 (6)	1	93·85	54·91	
9	26·66	57·35	{ Q_2 (5) / Q_1 (4)	5	95·59	49·72	P (8)
7	28·58	51·50	Q_2 (4)	1	96·08	48·28	
7	29·27	49·41	Q_1 (3)	1	97·81	43·12	P' (10)
7	30·39	46·00	Q_2 (3)	5	98·77	40·28	
6	31·25	43·38	Q_1 (2)	1−	02·24	29·96	
6	31·93	41·81	Q_2 (2)	1	03·19	27·12	
5	32·57	39·36	Q_1 (1)	2	03·64	25·81	P (9)
8	33·04	87·94	Q_2 (1)	1	09·91	07·20	
2	34·45	33·63		1	10·69	04·90	
2	39·35	18·75		1	11·97	01·12	P (10)
2	44·38	08·64		6	12·56	17199·42	
1	46·97	17395·67		1	16·39	88·09	
2	47·58	98·96	P (2)	1	19·25	79·65	
				1	20·67	75·46	P (11)

The relations found to exist between these six series are exhibited graphically in fig. 4 in the same manner as before. It may be well to point out, however, that the representation given in the figure and also the formula coefficients are to a large extent dependent upon the numeration adopted, and an alteration in the latter, which is in some cases open to question, would shift the series vertically in the diagram and considerably alter the appearance of the system.

Table VI.

Coefficients in Formulæ for λ 5730 Series.

Residuals.

Series.	m^0.	m.	m^2.	m^3.	m^4.	$(0-C) \times 100$.
---	---	---	---	---	---	1.	2.	3.	4.	5.	6.	7.	8.	9.	10.	11.
B	17420·56	+30·691	+0·0947	+0·16910	−0·012580		−1	0	−1	+3	−5	−2	+3			
Q₁	17437·29	+1·150	+0·8788	+0·05000	−0·006750	0	0	0	0*	+38†	0	0				
Q₂	17436·40	+0·448	+1·1740	−0·08567	—	0	0	0	+1	+7*	0	0				
P	17453·10	−32·333	+1·5760	−0·10008	+0·001380		0	+4	−2	+4	−1	0	−1	−4	+3	(+33)
R'	17436·76	+29·589	+1·0855	−0·09951	—	+1?	−1	−2	0	+5	0	−3	(−2½)			
P'	17437·28	−29·088	+0·8703	+0·08410	−0·006542		+3	−3	−2	−5	0	+1	+1	+1	+1	

* Blend.

† May be a blend with R'(1). Neglected in obtaining formula.

? This residual refers to Q₁(6), the intensity of which seems abnormally high, suggesting that R'(1) may possibly be superposed on it.

Residuals in brackets refer to very faint lines, the identification of which is not regarded as certain, and which have been disregarded in obtaining the formulæ.

The six series fall into three pairs, of P, Q and R types respectively, and at · first sight it would appear natural to regard them as two complete normal families. There are several objections to this view however, the chief of
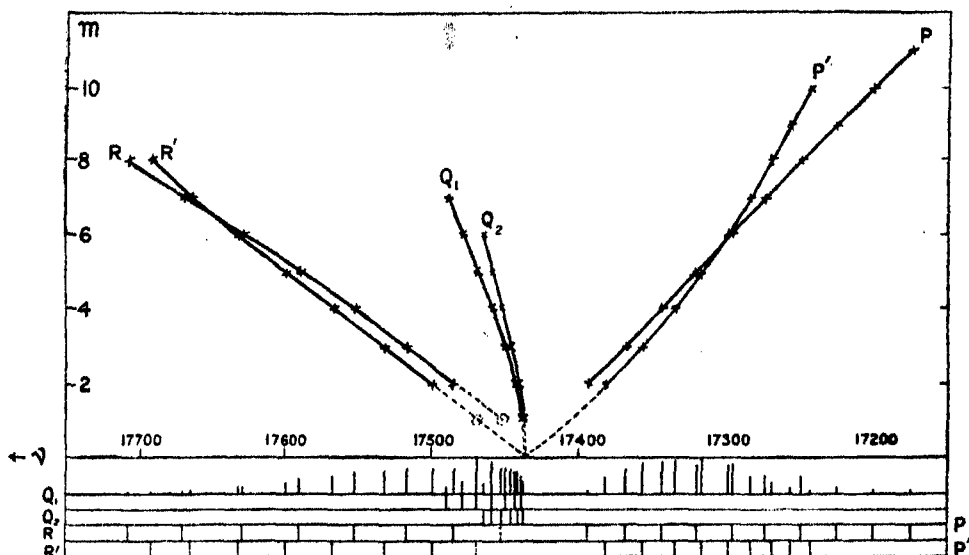
Fig. 4.—Helium band at λ 5730.

which is that the two Q series converge almost to the same wave-number, whereas the two values of ν_0 derived from P, R and P', R' (see figure) differ by no less than 14 units. The actual figures may serve to make the point clearer, and are as follows :—

$$Q_1(0) = 17437 \cdot 3, \qquad Q_2(0) = 17436 \cdot 4.$$

$$P(0) = 17453 \cdot 1, \quad c_0 = 16 \cdot 2, \quad \therefore \nu_0 = 17436 \cdot 9,$$

$$R(0) = 17420 \cdot 6, \quad c_0' = 15 \cdot 3, \quad \therefore \nu_0 = 17435 \cdot 9,$$

$$P'(0) = 17437 \cdot 3, \quad c_0 = 15 \cdot 0, \quad \therefore \nu_0 = 17422 \cdot 3,$$

$$R'(0) = 17408 \cdot 4, \quad c_0' = 13 \cdot 5, \quad \therefore \nu_0 = 17421 \cdot 9.$$

The numbering of P' and R' is here not the same as in the Tables and figure, but that appropriate to the above view, so that the formula coefficients differ from those tabulated. The mean value of ν_0 derived from P and R, 17436·4, is identical with $Q_2(0)$, but the corresponding value from P' and R' is 17422·1, 15·2 units from $Q_2(0)$ and 14·3 from $Q_1(0)$. The discrepancy remains however the numeration is varied, and one is bound to conclude that there is a relative displacement between the Q series and the other two. Such a complication is to be avoided if possible, and a means of doing · so is suggested by the results obtained in the preceding sections. We there established the existence of P' series running approximately parallel to the

P series, but extrapolating to ν_2 instead of to $(\nu_0 + c_0)$. The apparently displaced P series of this group fulfils these conditions very closely (see Table VI and fig 4). Moreover, the associated R series also extrapolates to ν_0 and runs parallel to the normal R series, so that it must be regarded in a similar way. This leaves the extra Q series as the only quite anomalous feature of the band, and is therefore thought to be a much more satisfactory method of representation than that first proposed. The values obtained for ν_0 from P' and R' now become 17437·3 and 17436·8, in excellent agreement with those derived from Q_1, Q_2, P and R.

The existence of two Q series is a puzzling feature of this band, for they are so close together that it is impossible to say which of them is associated with the normal P and R branches. It is true that the mean ν_0 determined from the latter agrees exactly with $Q_2(0)$, but $Q_1(0)$ only differs from this by 0·9 unit, by no means a large discrepancy in the light of our experience in previous cases. Other evidence available is equally indecisive; for example, there appears to be some connection between P' and Q_1 (evident from the coefficients), and also between R' and Q_2 (see below), so that which is the normal and which the additional Q series remains in doubt. An attempt has been made to fit them both by one formula, in which m may have both positive and negative values, but this appears to be definitely impossible.

As mentioned above, there seems to be a relation between Q_1 and P', in view of the remarkable similarity of the formulæ (except for the coefficients of m, which determine the type of the series), and again between Q_2 and R'. The latter appears when the differences $R'(m) - Q_2(m)$ are formed; these are found to be an approximately linear function of m, suggesting that if the formulæ had been exact the coefficients would have shown a similar correspondence to Q_1 and P'.

The question of missing lines is of much theoretical interest, and the position with regard to this band may be summarised thus :—

Series.	First observed line.	Remarks.
R	$m = 2$	R (1) would fall exactly on Q_2 (4), but the intensity of the latter seems normal.
Q_1	$m = 1$	The vertex of the parabola representing this series is nearer $m = -1$ than $m = 0$, which suggests that the first observed line may be $m = 2$.
Q_2	$m = 1$	The numeration here seems fairly well established.
P	$m = 2$	P (1) is definitely absent.
R'	$m = 2$	R' (1) may be present, as it would fall on Q_1 (5), which shows a large residual, and is abnormally strong.
P'	$m = 2$	P' (1) is definitely absent.

The observations are thus in good accordance with the theory, which demands that P(1) and R(1) should be absent if Q(0) does not occur. The theoretical significance of the P′ and R′ branches is at present unknown, but it may be noted that in the bands λλ 6400 and 4546 the line P′(1) is present, whereas here it is absent.

The initial and final values of the amount of inertia, calculated from the P and R branches as before, are $1·71 \times 10^{-40}$ and $1·80 \times 10^{-40}$ grm.-cm.[2]. These are a little lower than the corresponding results for the other two bands, but of quite the same order, so that it is unnecessary to suppose that we are dealing here with quite another type of molecule. The structural differences between the bands may reasonably be attributed to a difference between the changes of internal configuration involved. No other band resembling λ 5730 has been detected on the plates available, which cover the region λλ 6500 to 3350, but there are several regions where detection might be difficult.

Discussion of Results.

It has been shown in the preceding sections that the quantum theory of band spectra is capable of accounting in a very simple manner for the structure of the helium bands under consideration. Moreover, it explains their unusual appearance as due to an unusual intensity distribution necessarily resulting from the low atomic weight of helium. But the agreement with observation is not perfect ; deviations from the parabolic formulæ demanded by the theory are commonly met with in band series, and are in fact exceptionally large in the case of these helium bands. The observational evidence in favour of the theory is very strong, and its general validity can hardly be questioned, but it should be capable of modification or extension in order to take into account these deviations, or perturbations, as they have hitherto been called.

The general character of the perturbations is most clearly seen when the wave-number intervals between successive lines of a series are plotted against the corresponding values of m, the rotation quantum number characterising a given line. If the theoretical formulæ held exactly a straight line would thus be obtained, and we may roughly estimate the magnitude of the perturbation by the extent to which the graph departs from linearity. The general result which emerges from an examination of these curves is that the perturbation increases with m, and usually more rapidly for higher values of m. In fact, in several cases the interval reaches a maximum, and begins to diminish just as the series fades out. A similar tendency has been noted in the case of other bands,[*] but only for much larger values of m than in the present case.

[*] *E.g.*, Birge, 'Astrophysical Journal,' vol. 46, p. 92 (1917).

This feature of the perturbation immediately suggests as a possible cause the deformation of the molecule due to centrifugal force. In order to form an opinion as to whether the latter is likely to be large enough to produce the observed effects we may make a rough calculation as follows :—

Assuming two similar nuclei each of mass M at a normal distance $2r$ apart, the moment of inertia about an axis perpendicular to and bisecting the line joining them is I (say) $= 2Mr^2 = \dfrac{mh}{2\pi\omega}$. The centrifugal force on either

$$= M\omega^2 r = Mr\left(\frac{mh}{4\pi Mr^2}\right)^2 = \frac{m^2h^2}{16\pi^2 Mr^3}.$$

Now from the values for I already obtained, which average about $1\cdot8 \times 10^{-40}$, and taking $M = 7 \times 10^{-24}$ (mass of helium atom) the value of $2r$, the distance apart of the nuclei $= 2\sqrt{I/(2M)} = 0\cdot72 \times 10^{-8}$ cm. Substituting this value, the centrifugal force comes out as $m^2 \times 8 \times 10^{-7}$ dyne. We cannot directly determine the effect of this, since we are ignorant of the law of the attractive force binding the atoms, but we can perhaps gain some idea of its relative importance by comparing it with the force of repulsion between the two nuclei, which will be of the same order as the attractive force. Assuming a double charge on each, i.e., setting an upper limit to the force, the latter will be about $1\cdot8 \times 10^{-2}$ dynes. This is about 20,000 times the centrifugal force due to a one-quantum rotation state, but only 200 times that called into play when the rotation is 10 times as fast (corresponding to the last observed lines in the present bands). The known instability of the molecules emitting the bands under discussion lends support to the conclusion that for the larger values of m here encountered the centrifugal force may quite possibly be great enough to cause an appreciable deformation of the molecule, with consequent deviations from the theoretical formulæ for the wave-numbers.

It is interesting to note, in passing, that the above considerations may serve to explain the relatively large deviations in the case of helium as due to the relatively small mass and size of the molecules, together with their unstable character. Larger and heavier molecules will experience smaller centrifugal forces for corresponding values of the rotation quantum, and if further they are more stable, will be less deformed in proportion.

Such a deformation may affect the radiated frequency in one (or both) of two ways, which correspond to the two terms composing the expression for the energy of the molecule, namely, the internal energy (comprising K.E. and P.E. of the nuclei and electrons), and the rotational energy. In other words, either ν_0 or I, or both, may vary with m. In the absence of any precise knowledge of the molecular structure we cannot expect to account in detail

for the observed facts, but it seems possible to draw some general conclusions
which are not without interest.

Whatever the exact effect of the supposed centrifugal forces, the energy of
a molecule will depend partly upon its internal configuration and partly upon
the rotation quantum number. Let the energy prior to a configuration change
be $hF(m)$ and that subsequent to the change be $hf(m)$. Then, assuming the
three series to originate in the manner already described, we should have

$$R(m) = F(m) - f(m-1),$$
$$P(m) = F(m-1) - f(m),$$
$$Q(m) = F(m) - f(m),$$

also
$$Q(m-1) = F(m-1) - f(m-1).$$

Whence the following relation should be satisfied :—

$$R(m) + P(m) = Q(m) + Q(m-1).$$

This combination principle, which is due to Heurlinger, has been tested for
a number of bands ; in some cases it appears to hold exactly (e.g., for hydro-
carbon band λ 4300), but in others (e.g., H_2O, MgH_2), a deviation appears for
large values of m. The extent to which it applies to the bands $\lambda\lambda$ 6400 and
5730 may be seen from Table VII, which shows the values of $(R)\ m + P(m)/2$
and $Q(m) + Q(m-1)/2$, together with the differences between these quantities.
In the case of λ 5730, where there are two Q series, the test has been made
on each in turn. The relation is evidently far from exact in these cases, and
the departure from it is quite systematic, increasing in general with m. Since
the combination principle would not be invalidated by the existence of
deformation due to centrifugal force, we conclude that the latter is not
competent to produce the whole of the observed deviations from the theory.

The intensity distribution in band series is a point of some theoretical
interest, since it leads to an estimate of the distribution of rotational velocities
amongst the molecules. The plates on which the present work is based are
not very suitable for intensity estimations, as all the stronger lines are
considerably over-exposed, but so far as can be judged the intensity distribu-
tion is fairly normal. That is to say, there is a maximum two or three lines
from the beginning of the series, then four or five lines of fairly uniform
intensity, and finally a rather rapid falling off as the end of the series is
approached. Having regard to the unusually small number of lines
developed, this is comparable with the distribution in " ordinary " band
series, except that the latter do not in general fade out so suddenly. The
cause of this peculiarity in the helium bands may be that for the higher
rotational velocities the molecule is approaching an unstable condition.

If it were merely a question of whether the molecules possessing these larger velocities were sufficiently numerous to be detected one would expect a more gradual falling off in intensity.

Table VII.—Test of Combination Principle.

Band λ 6400.

m.	I. $\dfrac{R(m) + P(m)}{2}$	II. $\dfrac{Q(m) + Q(m-1)}{2}$	I–II.
2	15624·30	15623·14	+1·16
3	23·30	21·57	+1·73
4	21·82	19·21	+2·61
5	19·68	15·92	+3·76
6	16·88	11·74	+5·14
7	13·12	6·71	+6·41

Band λ 5730.

m.	III. $\dfrac{R(m) + P(m)}{2}$	IV. $\dfrac{Q_1(m) + Q_1(m-1)}{2}$	V. $\dfrac{Q_2(m) + Q_2(m-1)}{2}$	III–IV.	III–V.
2	17438·72	17441·37	17439·63	−2·65	−0·91
3	42·39	46·40	43·65	−4·01	−1·26
4	47·68	53·38	48·75	−5·70	−1·07
5	54·45	62·32	54·43	−7·87	+0·02
6	62·14	72·50	60·10	−10·86	+2·04
7	70·40	83·40	—	−13·00	

Note.—In the case of λ6400 the differences (I–II) would be considerably smaller if the Q series were numbered one higher throughout, but would still show a strong systematic variation. The agreement between the empirical and theoretical formulæ for this series, however, supports the numeration adopted.

The differences III–IV would also be reduced by a similar change of numeration, but again the systematic variation would remain. In this case the coefficients of the empirical formula for Q_1 seem to suggest that such a change may be necessary.

This question of the distribution of angular velocities has been investigated theoretically by Kemble,[*] who finds that the intensity maximum of the band should correspond to an angular velocity ω determined by the relation $I = RT/\omega^2 N$, where R is the gas constant, T the absolute temperature, and N the number of molecules per gramme-molecule. By substituting $I\omega = mh/2\pi$ this reduces to

$$ m^2 = \frac{4\pi^2 IRT}{h^2 N} = \frac{RT}{hN \cdot 2c_0} \text{ since } c_0 = \frac{h}{8\pi^2 I} $$

$$ = \frac{0\cdot68\,T}{2c_0} \text{ approx., when } c_0 \text{ is expressed in cm.}^{-1}. $$

[*] 'Phys. Rev.,' vol. 8, p. 689 (1916).

For the helium bands $2c_0$ is about 30 cm.$^{-1}$; T is not known, but is not likely to be much above room temperature. Putting it at 300° K we find $m = 2\cdot6$, i.e., the maximum should occur at about the second or third line, or perhaps a little farther from the beginning of the series if T has been under-estimated. The intensity estimates are too rough to permit of an exact verification, but the predicted result is of the right order.

One difficulty, hitherto passed over, calls for consideration, namely the assumed existence of a molecule of helium ; it is a necessary assumption, for the moments of inertia found are much too large to refer to a helium atom. In this connection Lenz* has made the plausible suggestion that when one of its electrons is close to the nucleus and the other far removed (i.e., in an outer orbit) the helium atom is approximately equivalent to a hydrogen atom so far as electrical forces are concerned, and two such atoms may unite to form an unstable helium molecule of similar type to the hydrogen molecule. Whatever the precise constitution of the helium molecule, there is no doubt of its instability. Its development seems to require special conditions of pressure and electrical excitation, and is greatly favoured by absence of all impurities.†

Granted that a molecule of helium may exist, the theory accounts for the bands as arising from a simultaneous change of internal and rotational energy. The nature of the former change cannot be directly inferred from the data here presented, but it is probably a change in the configuration of the electrons, since the resulting frequencies ν_0 are of the same order as for Fowler's series of doublet bands, which are distributed according to the ordinary law of line series. If nuclear vibrations can occur in this case, which the instability of the molecule renders somewhat doubtful, they are likely to be of a lower order of frequency, and may be expected to give rise to bands in the near infra-red region. It is hoped that a search for these may be undertaken in the near future. The pure rotation spectrum corresponding to the present bands will lie in the far infra-red, round about 100μ, and will consequently be difficult to observe.

Application of Results.

It is thought that the results obtained may be of service in several ways. The first application will naturally be to the remaining bands in the spectrum, although these appear to show some marked differences in structure. They

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* 'Verh. d. D. Phys. Ges.,' vol. 21, p. 632 (1919).

† Some interesting observations in this connection will be found in a paper on "Radiation and Ionisation in Helium," by Horton and Davies, 'Phil. Mag.,' vol. 42, p. 746 (1921).

are nearly all included in Fowler's doublet series; the double heads are probably of Q type, and are accompanied in each case by a P series, but not by an R series, so far as can be ascertained by inspection. The separation of the two heads is much greater than in the case of the λ 5730 Q series.

There is little doubt that the secondary spectrum of hydrogen is due to the hydrogen molecule, and it may therefore be expected to show the general features of a band spectrum together with some of the special features which distinguish the helium bands. The smaller moment of inertia which we may assume the hydrogen molecule to possess, however, should lead to a larger frequency interval between successive members of a series, and probably also to the development of a less number, although in this connection the relative stabilities of the two molecules will have an influence. Either factor would make the series relationships more difficult to detect, but a beginning has already been made,* and it seems reasonable to hope that further progress may be facilitated by the present observations.

The infra-red absorption bands of HF, HCl and HBr,† which have been the subject of much discussion during the last few years, present features which it is interesting to examine in the light of the present results. They appear to consist of P and R type series (but no Q branch) of a normal character, except that only one line is missing from the middle of the band, whereas on the simple theory missing lines should occur in pairs. Kratzer‡ has put forward an explanation of this, and reaches the conclusion that in emission bands the line due to the transition $1 \to 0$, *i.e.*, R(1), should be missing, and in absorption bands that corresponding to $0 \to I$, *i.e.*, P(1). It remains to be seen whether this is confirmed by experience in the case of these bands, for no adequate data relating to their emission characteristics are available, but certainly does not appear to hold in the case of helium. An alternative possibility which is suggested by the present results is that these absorption bands may be of the P' and R' type, in which case the missing line would be $P'(0) = R'(0) = \nu_0$. This would account for the peculiarity referred to, but until some theoretical explanation of the P' R' system is forthcoming the question must be left open.

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* Fulcher, 'Astrophysical Journal,' vol. 37, p. 60 (1913).

† Imes, 'Astrophysical Journal,' vol. 50, p. 251 (1919); Colby and Meyer, 'Astrophysical Journal,' vol. 53, p. 300 (1921).

‡ 'Z. f. Physik,' vol. 3, p. 289 (1920).

Summary.

Grating photographs of three of the principal helium bands have been measured and analysed, with the following results :—

(1) Tables showing wave-lengths, intensities, wave-numbers and allocation to series are given, also diagrams exhibiting the structure of the bands.

(2) The chief features of their structure are shown to be accounted for by the quantum theory of band spectra, a brief *résumé* of which is given.

(3) In each of the three bands a new type of series is found which, although closely related to the others, has not yet received a theoretical explanation. Other departures from the theory are also noted.

(4) It is concluded that the spectrum is due to an unstable helium molecule, having a moment of inertia of about 1.8×10^{-40}grm.-cm.^{2}

On the Molecular Scattering of Light in Water and the Colour of the Sea.

By C. V. RAMAN, M.A., Hon. D.Sc., Palit Professor of Physics in the Calcutta University.

1. *Introduction.*

The theory that the light of the sky owes its origin and colour to diffraction by the molecules of the atmosphere is now established on a firm experimental basis by the brilliant work of Cabannes and of Lord Rayleigh on the scattering of light by dust-free gases, and by the measurements of the transparency of the higher levels of the atmosphere in the visual region of the spectrum, which have yielded results in close agreement with the calculated values. It is the purpose of the present paper to point out the part played by molecular diffraction in another of the great natural optical phenomena, that is, the colour exhibited by large masses of clear water when
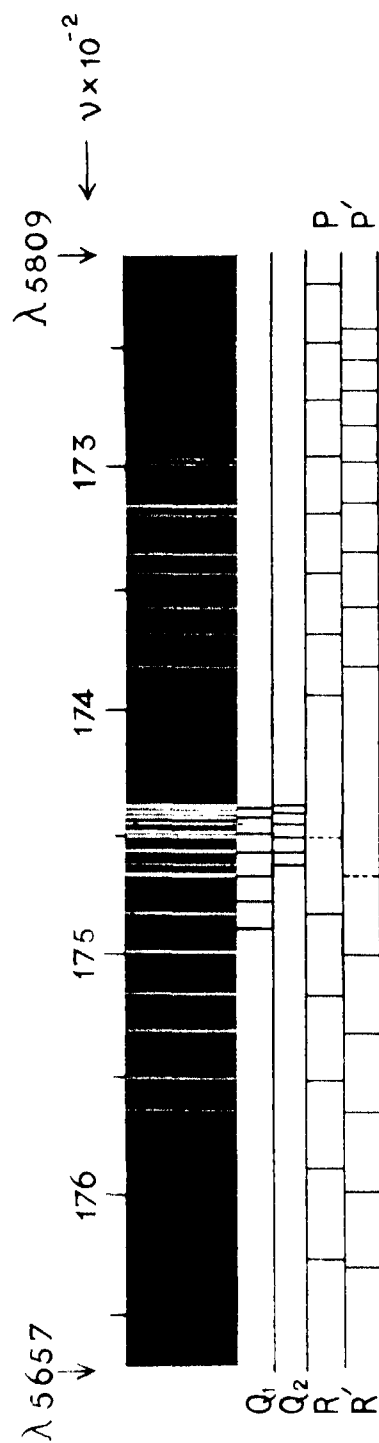
illumined by sunshine and viewed from above, the depth being so great as to provide a perfectly black background for observation. The subject at present is in a somewhat peculiar position, as even on the question of the reality of the phenomenon there appears to be a divergence of opinion. On the one hand, we have the following view expressed by so eminent an authority as the late Lord Rayleigh :* "We must bear in mind that the absorption, or proper, colour of water cannot manifest itself unless the light traverses a sufficient depth before reaching the eye. In the ocean the depth is, of course, adequate to develop the colour, but if the water is clear, there is often nothing to send the light back to the observer. Under these circumstances, the proper colour cannot be seen. The much-admired dark blue of the deep sea has nothing to do with the colour of water, but is simply the blue of the sky seen by reflection." On the other hand, observers familiar with the sea, such as J. Y. Buchanan, of the " Challenger " expedition, who have had very wide opportunities for study, have published detailed descriptions which support an entirely contrary view.† An admirable *précis* of the literature on the whole subject has been recently published by Prof. W. D. Bancroft.‡ From a perusal of this very convenient summary, and from the account given in Kayser and Runge's ' Handbuch,' it would appear that the general trend of opinion is that, so far as there is any real effect to be explained at all (that is, apart from reflected sky light) the colour of water is due to absorption, the return of the light from the depths of the liquid being due to suspended matter in it. During a recent ocean voyage, the present author has had an opportunity of making some observations which show that the view indicated above is entirely inadequate. It is proposed in this paper to urge an entirely different view, that in this phenomenon, as in the parallel case of the colour of the sky, *molecular diffraction* determines the observed luminosity and in great measure also its colour. As a necessary preliminary to the discussion, a theoretical calculation and experimental observations of the intensity of molecular scattering in water will be presented.

2. *Theory of Molecular Diffraction of Light in Liquids.*

In the theory of the molecular scattering of light by gases developed by the late Lord Rayleigh, a very simple relation is established between the refractivity of the medium and the energy scattered laterally by it. These quantities are calculated on the assumption that the scattered waves originating from the individual molecules are, except in the direction of the

* ' Scientific Papers,' vol. 5, p. 540.
† ' Nature,' July, 1910, p. 87.
‡ ' Franklin Inst. Journal,' 1919, and also reprinted in ' Chemical News,' 1919.

propagation of primary waves, in entirely arbitrary phase-relationships and that their energy-effects may therefore be treated statistically as additive. The justification for this view, namely, that the molecules are in irregular order and possess large thermal movements, has been further discussed by Sir Joseph Larmor[*] and the present writer.[†] Experiment shows that the Rayleigh law of scattering is in good agreement with observation, even when the gas is very dense or highly compressed. On the other hand, in the case of liquids, the spacing of the molecules is far closer and their freedom of movement much less, and we should no longer be justified in making the same assumptions. A gramme-molecule of steam occupies at 100° over 1600 times the volume which an equal mass of water would occupy, and it is clear, *prima facie*, that volume for volume, water would not scatter light 1600 times as strongly as pure steam, but only in a lesser degree. The question is, by how much less?

A method of approach to the problem of molecular scattering, which is somewhat different from Rayleigh's and which enables the case of liquids to be included, is the " theory of fluctuations " developed by Einstein and Smoluchowski, and used by the latter especially to elucidate the optical phenomena observed in the vicinity of the critical state.[‡] In this theory, the medium is regarded as undergoing small local variations of density owing to the irregular movements of the molecules, and the result of these fluctuations of density is that a certain proportion of the incident light is scattered. The formula developed is quite general and it is shown that the intensity of the light diffused by a cubic centimetre of the fluid at right angles to the direction of the incident rays is

$$\frac{\pi^3}{18} \cdot \frac{\beta}{\lambda^4} \cdot \frac{RT}{N} \cdot (\mu^2-1)^2 (\mu^2+2)^2.$$

λ is the wave-length, β the compressibility of the substance, μ its refractive index, and R, T, N, have the usual significance attached to them in the kinetic theory.[§] In the case of gases, β is simply the reciprocal of the pressure, and μ being nearly unity, the expression reduces identically to Rayleigh's formula. The result may be applied equally well to find the intensity of the light scattered in liquids. For air under standard conditions,

$\beta = 0.987 \times 10^{-6} \text{cm.}^2\text{dyne}^{-1}$, T = 273° and $\mu = 1.000293$.

For water at 30°, $\beta = 48.9 \times 10^{-12}\text{cm.}^2\text{dyne}^{-1}$, T = 303° and $\mu = 1.337$. From

[*] ' Phil. Mag.,' January, 1919.

[†] ' Nature,' May 1, 1919.

[‡] For references, see Perrin's ' Atoms,' Chapter V, authorised translation. Also Epstein, ' Ency. Math. Wiss.,' vol. 3, p. 520 (" Spezielle Beugungsprobleme ").

[§] R and N refer to a gramme-molecule and not to unit volume.

these data, it is readily found on calculation that, volume for volume, water at 30° should scatter light 159 times as strongly as dust-free air under standard conditions.

It should be remembered that in the theory on which'the foregoing result is based, the scattering considered is merely that associated with the ordinary refractivity of the medium, considered along with the non-uniformity of optical density resulting from molecular movement. The light scattered in a direction perpendicular to the incident rays should be completely polarised. This result holds even when the regions in which the small density fluctuations occur are not of dimensions small compared with the wave-length.* It is a point worthy of notice that according to the formula, the scattering power of liquids is proportional to the absolute temperature, apart from the changes which would result also from the variation of compressibility and refractive index with temperature.

3. *Experimental Study of Molecular Diffraction by Water.*

To determine whether the intensity of light molecularly scattered in water, as indicated by the theory, is at least of the same order of quantities as in experiment, some observations have been made by the writer. On examination, the ordinary town-supply water as taken from the pipes showed a very strong scattering when a beam of light was sent through it. The track was practically white and showed innumerable motes floating about in the water. Repeated filtration through several thicknesses of Swedish filter paper made an improvement, the track of the beam being now of a bluish colour, and a still better result was obtained when an earthenware filter was used. Suspended matter was, however, still in evidence and the track was also much brighter when viewed nearly in the direction of the source than when seen transversely or in the opposite direction. A somewhat casual attempt was then made to clear the water by adding alkali and alum and thus throwing out a gelatinous precipitate of hydroxide. This made a further improvement, but small particles of the precipitate remained floating about, apparently because the depth of the water was insufficient, and the appearance of the track of the beam was not very prepossessing. The next attempt was made with ordinary distilled water which had been prepared without any special precautions and stored in the chemical laboratory. This gave immediately a much smaller intensity of light scattering than the tap-water had done after several attempts at filtration. For purposes of observation, the distilled water was put into a stoppered glass bottle with square sides and allowed to stand.

* Rayleigh, 'Scientific Papers,' vol. 5, p. 547.

Test-observations from day to day of the scattered beam with a double-image prism and a set of Wratten colour filters shqwed a progressive improvement. After about a fortnight's standing, the track of the light was hardly conspicuous unless a dark background was provided for it to be viewed against, and the defect of polarisation at the violet end of the spectrum was much less striking than it was when the observations were begun. Small motes were still to be seen glistening in the liquid, particularly when it was viewed nearly in the direction of the source, but the track of the beam viewed transversely was of a blue colour and it was judged that the greater part of the observed luminosity was probably due to the water itself.

For a quantitative estimate, the brightness of the beam in the water was compared directly with that of its track in saturated ether vapour. The latter was contained in a pear-shaped bulb with a long neck which was covered over with black paint and formed the "black cave" against which the light scattered by the vapour was observed. The bottle and the bulb were set side by side and a parallel beam of light passed through both. An Abney rotating sector was placed in front of the water-bottle and the opening of the sector varied till the tracks appeared to be of equal intensity in both vessels as judged visually. The opening of the sector gave the ratio of intensities, a correction being made for the loss of light by reflection in the passage of the direct and scattered pencils through the glass walls. It is not pretended that the determinations made in this way were anything more than approximate estimates; it was thought that more elaborate measures could well be reserved till thoroughly satisfactory samples of "mote-free" water could be obtained. The scattering of light in saturated ether-vapour has been measured by comparison with air by Rayleigh, and shown to be strictly in proportion to the square of its refractivity. Using this result, the observations showed that the scattering power of the sample of water used was 175 times that of dust-free air under standard conditions. This, though not agreeing exactly with the theoretical value is only slightly in excess, and the difference is not more than can reasonably be explained as due to residual suspended matter present in the sample of water used.

The light scattered by water in a direction transverse to the incident beam was found to be strongly, but not quite completely, polarised. It seems quite likely that the imperfect polarisation is really a characteristic of water, and not merely due to presence of residual suspended matter. More complete measurements of the defect of polarisation have, however, been held up till a thoroughly pure sample of water is obtained.

4. *Molecular Scattering and Transparency of Water.*

Since the energy of the light laterally scattered is derived from the primary beam, there must result a certain attenuation in the intensity of the latter in its passage through the liquid, the magnitude of which may be readily calculated from the coefficient of scattering. The expression for the intensity of the transmitted beam is $I = I_0 e^{-\alpha x}$, where x is the length of path traversed through the liquid and

$$\alpha = \frac{8\pi^3}{27} \cdot \frac{\mathrm{RT}\beta}{\mathrm{N}\lambda^4} \cdot (\mu^2 - 1)^2 (\mu^2 + 2)^2.$$

As in the case of atmospheric scattering, we may expect that the coefficient of attenuation α will exactly indicate the observable transparency of the medium *in those parts of the spectrum for which it does not exercise any selective absorption.* From the data already given and the known values of R, T and N, α may readily be determined for any value of the wave-length.

From the observations of various experimenters, it is known that water exercises a selective absorption on the longer wave-length side in the visible spectrum. The most reliable measurements of any hitherto made appear to be those of Count Aufsess, quoted in Kayser's 'Handbuch.' This experimenter used double-distilled water, and convinced himself that it was free from suspended matter: it was found by him that the selective absorption in the visual region practically ceased for wave-lengths less than $558 \mu\mu$. For the two wave-lengths $522 \mu\mu$ and $494 \mu\mu$, Aufsess gives us the coefficient of absorption 0·00002. For these two wave-lengths, the coefficient of attenuation α, calculated from the formula given above, is respectively 0·000022 and 0·000029. The agreement of observation and theory is significant, and it would be interesting if further accurate measurements for different wave-lengths up to the extreme violet end of the spectrum were available, so that the increase of the coefficient of attenuation inversely as the fourth-power of the wave-length could be tested. It would also be interesting to determine by careful experiment whether the intensity of the light scattered by water exactly follows the fourth-power law; if the selective absorption in the longer wave-lengths is accompanied by any selective scattering, deviations from the λ^{-4} law may be expected to appear in that region of the spectrum.

5. *Luminosity of Deep Water due to Molecular Scattering.*

Since, in round numbers, water diffuses light 160 times as strongly as an equal volume of air, a layer of the liquid 50 metres deep would scatter approximately as much light as 8 kilom. of homogeneous atmosphere, in

other words, it should appear nearly as bright as the zenith sky. This rough calculation, however, omits to take into account two important factors, the diminution in the intensity of sunlight before it reaches the level of the water, and its further attenuation in the passage through the liquid, and also the loss in intensity of the scattered light before it re-emerges from the depths. It is the two last factors just mentioned which, together with the magnitude of the scattering itself, ultimately determine the total observed luminosity of an ocean of liquid of very great depth. Neglecting the effect of self-illumination within the liquid, and also the contribution which is made by diffuse skylight, which enters the water and is then subsequently re-scattered within the liquid—both of which may, in certain circumstances, rise to importance—the observable luminosity of a very deep layer of liquid may be readily calculated. For simplicity, we shall consider a case in which the altitude of the sun is sufficiently great to enable its rays within the water to be treated as approximately vertical in direction, and the intensity of the light scattered will also be assumed to be observed in an approximately vertical direction, *e.g.*, by an observer in an aeroplane flying at some height above the water. The coefficient of scattering in such a case will be twice as great as when the scattering is observed laterally. Denoting it by $2B/\lambda^4$, and the coefficient of absorption of light in water by γ, the total observed luminosity is given by the integral

$$\frac{2B}{\lambda^4} \int e^{-2\gamma x} \, dx,$$

x being the depth of any layer. For a sufficiently great depth, this reduces to $B/\gamma\lambda^4$. For the case of pure water, the values of γ are taken from the determinations of Count Aufsess for wave-lengths up to 522 $\mu\mu$, and, for shorter wave-lengths, we may take them to be the same as the value of coefficient of attenuation α given by theory. The value of B is in round numbers 160 times the coefficient of lateral scattering by dust-free air. From these data, and making an allowance for the diminution of the solar intensity in transmission through the atmosphere as on an average day, the total luminosity of deep water for different wave-lengths is expressed in Table I in terms of the kilometres of dust-free air at atmospheric pressure, which would, by lateral scattering of full sunlight, give an equal effect.

If we take the scattering by 8 kilom. of dust-free air as the standard and compare with it the figures shown in Table I, it is seen that in the light returned by the water practically all the red is cut out, the orange and yellow are quite feeble, but the green is greatly enhanced, and also the blue, indigo, and violet, but to a considerably less extent. The standard of comparison

Table I.—Luminosity of Deep Water.

λ in μμ.	658	622	602	590	579	558	522	494	450	410
Equivalent kilo-metres of dust-free air.	0·4	0·5	0·7	1·4	2·5	3·0	50	40	24	15

(scattering by dust-free air) being itself of a blue colour, it is clear that the cutting out of the red and the enfeeblement of the orange and yellow would result in the colour of the light scattered by the water being a highly saturated blue. The enfeeblement of the orange and yellow would, however, considerably diminish the visual intensity, which, at a rough estimate, would probably not exceed two or three times that of the zenith sky.

It will be understood from the figures given in Table I that the blue colour of the light scattered by the water arises primarily from the operation of the Rayleigh λ^{-4} law, the absorption of the red and yellow regions of the spectrum in the water resulting merely in the colour being more *saturated* than it would otherwise be. If the figures entered in the columns of Table I had represented ratios of comparison with *white* light, the presence and predominance of the green would result in the perceived colour being a greenish blue, and not a deep blue colour. In other words, the blue colour of the scattered light is really due to diffraction, the selective absorption of the water only helping to make it a fuller hue.

6. *Colour of the Sea not due to Reflected Sky-light.*

There does not appear to be any way of escape from the consequences of the Einstein-Smoluchowski theory of molecular scattering worked out in the foregoing pages. Postulating an ocean of clear water, and of great depth, we have necessarily to accept the consequence that under the illumination of the sun's rays it would scatter light of a colour greatly transcending the light of the sky in the saturation of its blueness, and, also, unless the transparency of the water is much inferior to that of the pure liquid as observed in the laboratory, comparable with the light of the sky in its brightness. There is ample evidence regarding the great transparency of oceanic waters, at least under normal conditions, in calm weather. Writing of the mid-Pacific, J. Y. Buchanan states* that a metal plate only 4 inches by 4 inches, painted white and suspended at a depth of 25 fathoms (45 metres), was distinctly seen with sharply defined edges. The plate became indistinct at greater depths, but this was only on account of its smallness and want of steadiness, owing to

* 'Nature,' *loc. cit.*

the movement of the boat from which the observations were made. The plate was seen through the glass bottom of a floating tub, in order to eliminate the effect of ripples on the surface of the water. Buchanan adds that the colour of the column of the liquid, 25 fathoms in length, resting on the plate was a pale but pure ultramarine; that of the external and uninterrupted column surrounding it was of the same tone, but of many times greater intensity. He infers that the length of the uninterrupted column, which contributed to the luminous effect by diffusing sunlight upwards, must have been much greater than 25 fathoms. Buchanan's observations clearly indicate a high degree of transparency, and show that the colour of the sea really arises from a scattering of light upwards from within the water.

The statement by the late Lord Rayleigh, that the deep blue colour of the sea is merely due to reflected sky-light, has already been quoted in the introduction. We shall now proceed to examine the grounds urged in support of this view: "When the heavens are overcast the water looks grey and leaden, and even when the clouding is partial, the sea appears grey under the clouds, though elsewhere it may show colour. . . . One circumstance that may raise doubts is that the blue of the deep sea often looks purer and fuller than that of the sky. I think the explanation is that we are apt to make comparison with that part of the sky which lies near the horizon, whereas the best blue comes from near the zenith. In fact, when the water is smooth and the angle of observation such as to reflect the low sky, the apparent blue of the water is much deteriorated. Under these circumstances a rippling due to wind greatly enhances the colour by reflecting light from higher up. Seen from the deck of a steamer, those parts of the waves which slope towards the observer show the best colour for a like reason." The *facts* indicated in this quotation are, of course, quite correct; but the *explanations* given may well be questioned, and a closer examination shows that they require to be modified considerably.

Considering first the effect of clouds in the sky, careful observation shows that the presence of a cloud alters the appearance of the sea in two entirely distinct ways. In the first place, the water under the shadow of the cloud is screened from the direct rays of the sun, and the amount of light that can be diffused upwards from within the liquid is greatly diminished, and it must therefore necessarily appear darker. This feature is admirably shown in aeroplane photographs of water when the sky is clouded. In the second place, the presence of a cloud greatly increases the brightness of the part of the sky against which it is seen, and therefore also the brightness of its reflection in the surface of the water. In the case of an individual cloud, the apparent position of its reflected image on the surface of the water

(which depends on the position of the observer) and the position of the shadow (which is independent of it) may be entirely different. When the clouds are more numerous and the sky gets more or less completely overcast, the two effects occur together over practically the whole area of the water, and the result is that the brightness of the surface-reflection is considerably enhanced, and the brightness of the light diffused out from within the water made quite small. The appearance of the sea is therefore naturally completely altered, but this in no way indicates that the blue colour of the sea, as ordinarily seen when the sun shines full into it, is merely reflected sky-light.

The difference in the colour of the sea, when it is entirely smooth and when its surface is slightly ruffled, or even merely rippled, is, indeed, remarkable; closely connected with this effect is the difference in colour between the fore and back parts of an undulation on the surface of the water. Careful observation shows that the explanation for this suggested by Rayleigh is not adequate, and that the effect, or at least the greater part of it, really arises in another way. It is obvious that the light molecularly diffused within the water before it can emerge into the air must in part be reflected internally at the surface of the liquid. If the surface of the liquid be viewed very obliquely, that is in a direction nearly parallel to it, the only part of the diffused light which can reach the observer's eye is that which is incident at nearly the critical angle on the boundary between the two media, and of this a considerable part would be reflected internally, and the portion that emerges would also be greatly attenuated by the increased angular divergence of the scattered pencils. In the same circumstances, the external surface would reflect the low-lying parts of the sky almost completely, the incidence being nearly grazing. The diffused light from inside the water would thus be overpowered by the sky-reflection. When, however, the surface of the water is even slightly disturbed, the conditions are completely altered. The scattered light can emerge freely into the air through the parts of the surface that slope towards the observer, and to a lesser extent through the parts that slope away from him, so far as they are visible at all, the latter portions showing the reflections of the sky more conspicuously. The differences in colour that arise in this way, and are actually observed, are much greater than can be explained merely by reference to the difference between the different parts of the sky.

Again, as has been pointed out by Tyndall and Buchanan, the colour of the sea is best seen when looking almost vertically down on its surface. The effects seen in this way can hardly be influenced by sky-reflection, as the brightness of the zenith sky is relatively small, and the reflecting power of

water for normal incidence is only 2 per cent. Further, both of these writers describe observations made in circumstances in which the sky-reflection is eliminated altogether. One view that might perhaps be taken is that, while the colour of the sea is a real phenomenon which may be observed under suitable conditions, the appearance of the sea as a whole, as seen from the deck of a steamer, is largely determined by reflected sky-light. I think even this view would be a mistake. If it were true, the elimination of the reflection should result in the general appearance of the sea becoming impoverished. It will be shown later in the paper how this test can be applied, and the result is exactly the opposite. As a result of the discussion, we are thus led to the conclusion that the colour of the sea is a real phenomenon, that it is not due to reflected sky-light, and that the latter is merely a somewhat inconvenient disturbing factor in the observations.

7. *Colour of the Sea not due to Suspended Matter.*

It has been shown in the foregoing pages that pure water of the highest obtainable transparency is capable of exhibiting in its own body, as the result of molecular scattering, a blue colour of intensity amply sufficient to explain all that is observed in any actual case. There is a consensus of opinion among observers that the natural waters which show a deep blue are the most transparent of all. Nevertheless, in order to account for the observed return of the light from within the water, they have also agreed amongst themselves to supply a greater or less amount of suspended matter, according to the supposed requirements of theory! The position here is fairly analogous to that we find illustrated in regard to the theories of the colour of the sky. Ignoring the possibilities arising from the molecular structure of air itself (regarding which at least an early hint was given by Herschel), vesicles (!) of water were postulated. Subsequently dust-particles took their place, and were dispensed with only after it was recognised that the air itself was capable of explaining all that was observed; dust is now only a disturbing factor, the effect of which in favourable circumstances may be quite negligible. In the opinion of the writer, it would make for progress to adopt at once the position finally reached in the parallel case, and to recognise that the observed colour of the sea is primarily due to the water ·itself, and that suspended matter, if present at all in appreciable quantity, is to be regarded as a disturbing factor, of which the effect requires to be assessed in each individual case. As regards the deep blue or ultramarine colours of the oceanic waters, at any rate, there is good reason for believing that the observed luminous effect is not due to suspended matter in any appreciable degree. In order that suspended matter might have

a noteworthy optical effect, it should be present in a highly dispersed or colloidal form. Not only is this unlikely, in view of the actual marked transparency of these waters, which has already been remarked upon, but it would also be inconsistent with the coagulative property of the electrolytes present in the sea-water. As is well known, the colloidal matter brought down by the great rivers is thrown down when the fresh and salt waters mix, and practically none of it gets far out to sea. This is very prettily shown in sailing out from the mouth of a river or from the coast by the rapidly decreasing intensity of the Tyndall phenomenon shown by the sunbeams playing in the water. In the deep sea the Tyndall phenomenon can only be perceived if one looks down into the water in nearly the same direction as that in which the sun's rays enter the liquid. The tracks of the sunbeams can then be perceived going down into the water, and appearing by virtue of perspective to converge to a point at a considerable depth within it. This relative faintness of the Tyndall phenomenon in deep water is itself the best proof of the negligibility of any effect save that of molecular scattering. Reference may be made also to the observations of Tyndall,* who examined different specimens of sea-water, and found that, while the green seas showed suspended matter, the deep blue waters were very pure, and contained very little matter. Aitken,† speaking of the Mediterranean, mentions large white reflecting particles present in it; but, from the details mentioned in his paper, it is clear that he is referring to the greenish-blue regions near the coast, and not to deep-sea water.

As regards inland lakes, it is difficult to be very precise, as so much depends on the individual circumstances of each case, but it is more than likely that a detailed examination will show that, in the case of the very transparent deep blue waters, the influence of suspended matter is almost negligible. In this connection, it is useful to consider how suspended matter, if present, would influence the observed results. The quantity of suspended matter and the state of its dispersal are here both relevant. First, we shall consider the case of *very finely* dispersed matter, and note the changes that would occur as the quantity is increased. In Section 5, it has been shown that the total observed luminosity for any wave-length is proportional to the scattering coefficient, and varies inversely as the attenuation coefficient. In the region of the spectrum in which there is no selective absorption, both of these quantities would be increased in the same ratio, and hence the luminous effect would remain unaltered. In the region of selective absorption, the scattering would be increased without any

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* Quoted *in extenso* in Bancroft's paper, *loc. cit.*
† Bancroft's paper, *loc. cit.*

appreciable increase in the coefficient of attenuation. *Taking this into account, along with the figures given in Table I, we may draw the following* inference: (*a*) a *very small* quantity of finely dispersed matter would not appreciably alter either the colour or intensity; (*b*) a larger quantity of such matter would cause some increase in intensity, accompanied by a decrease in the saturation of the hue.

Suspended matter not very finely dispersed would operate in a different way. The first effect of increasing size of the particles would be the break-down of the λ^{-4} law as regards the intensity of the light scattered in any given direction. With a collection of particles of different sizes, the colour of the light scattered would be practically the same as the colour of the light incident on the particles in any given layer, and we should find the water exhibiting a greenish-blue or green colour according to the quantity of suspended matter. It must not be supposed that the presence of suspended matter necessarily increases the intensity of the light scattered upwards. This depends a good deal upon the nature and the size of the particles. If their diameter be not small compared with the wave-length, they would diffract light unsymmetrically, that is, scatter more strongly in the direction of the primary beam than in the opposite direction towards the source, and this would result in a diminution of the intensity of scattering in the latter direction. If, further, the particles are of a fairly uniform size, special polarisation effects would also be observed. It is, however, not necessary here to enter further into these details.

Finally, it should be remarked that in regard to the total quantity of light scattered upwards from the water, small changes in the quantity of suspended matter, if any, present in the water are of much less importance than variations of the transparency of the water arising from other causes, *e.g.*, the appearance of a very small quantity of organic matter in the water exercising a selective absorption in the blue region of the spectrum. This would greatly enfeeble the scattered light that emerges from the water, without much altering its colour.

8. *Polarisation and Colour Phenomena observed at Sea.*

According to the theory of molecular diffraction in liquids, the light scattered at right angles to the direction of the illuminating beam should be polarised. In attempting to test by observation at sea, other interesting effects are also noticed which will now be described.

As already remarked above, the reflection of sky-light at the surface of the water is an embarrassing feature in making observations of the colour of the sea. Its influence may, however, be eliminated in the following simple way:

Light reflected at the polarising angle from the surface of a liquid may be
quenched by observation through a suitably oriented nicol. Hence, by
observing a tolerably smooth patch of water through a nicol at the polarising
angle, the surface reflection may be got rid of. The nicol may be mounted at
the eye-end of a cardboard tube, so that it can be conveniently held at the
proper angle with the surface of the water and rotated about its axis so as to
get the correct position for extinction of the reflected light. During a recent
voyage, the writer made some observations by this method in the deeper
waters of the Mediterranean and Red Seas, and found that the colour of the
sea, so far from being extinguished when the sky-reflection is cut off, is seen
with wonderfully improved vividness and with saturated hues. Even when
the water is ruffled or when it is viewed more obliquely than at the polarising
angle, the nicol helps to weaken the sky-reflection. Further, as is well-
known, the light of the sky is itself strongly polarised, and this fact may in
favourable circumstances be used to practically eliminate sky-reflection from
the whole surface of the sea. For this purpose, the time most suitable is
when the sun has reached its maximum altitude, and the observer should stand
with his back towards the sun and view the surface of the sea through a nicol.
The part of the sky facing the observer has then its maximum polarisation,
especially the low-lying parts, and the amount of polarisation is further
enhanced when the light is reflected from the water at various angles of
incidence. By turning the nicol about its axis, the best position for extinction
should be found, and the whole surface of the sea will then be found to glow
with a vivid blue light emerging from inside the water. Part of this improve-
ment is also due to the fact that the nicol in great measure cuts off the
atmospheric haze which covers the more distant parts of the sea.

The obvious way of testing the light from the sea for polarisation, that is,
viewing it through a nicol and turning the latter about its axis, is interfered
with by the fact that the intensity of the reflected light also varies at the
same time and obscures the variation in the intensity of light diffused from
inside the water. Even thus, however, it is possible to observe the polarisa-
tion of the scattered light, the surface of the water appearing *less* blue when
seen through the nicol in one position than when viewed directly. Much
the better way of detecting the polarisation of the diffused light, however, is
to hold the nicol at the proper angle for extinguishing the surface-reflection
from the water, and to vary the azimuth of observation relatively to the
direction of the sun's rays entering the liquid. Striking changes in the colour
and intensity of the light diffused by the water will then be noticed. The
best time for making this observation is when the altitude of the sun is
moderately large but not too great. Obviously, if the sun's rays are too

nearly vertical, varying the azimuth of observation can make no difference. But when the sun's rays inside the water proceed at an angle to the surface, the variation of the azimuth of observation alters the relation between the direction of the primary beam and the scattered rays under test. When the observer has his back to the sun, he looks down practically along the track of the rays inside the water, and the scattered light reaching his eye is unpolarised inside the water and is not extinguished in any position of the nicol. The colour of the scattered light is then seen as a vivid but comparatively lighter blue. As the azimuth of the plane of observation is swung round, the intensity of the scattered light diminishes and its colour changes to a deeper blue, until finally when the observer nearly faces the sun,* the intensity of the scattered light is very small and it appears of a dark indigo colour. If the polarisation of the scattered light were complete and the direction of observation exactly transverse to that of the primary beams inside the water, the nicol would have completely quenched the light. This is, however, not actually the case, evidently because we have to deal not only with the scattering of the sun's direct rays inside the water, but also with multiply-scattered light, and also with the blue light of the sky which enters the water and is then re-scattered within it. It is evident that these contributions to the luminosity of the water would diminish the perfectness of the polarisation,† and would give a much darker blue than the primarily scattered rays.

The relatively deep colour of the secondarily scattered rays mentioned in the preceding paragraph is also prettily illustrated by observing the water on the shadowed side of the ship, where the sun's rays do not strike it directly. Such water shows a much darker and deeper colour than the contiguous parts exposed directly to the sun's rays. A similar explanation may be given of the deepening of the colour of the sea as the sun goes down. The lower the altitude of the sun, the more important is the contribution of sky-light re-scattered within the water to the observed luminous effect. The blue

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* He cannot, of course, exactly face the sun, as the reflection of the sun's rays from the surface of the water would then interfere with the observations. It is advantageous to choose a time when the altitude of the sun is such that these reflections are also quenched by the observing nicol. It should also be mentioned that the partial polarisation of the sunlight, when it enters the water obliquely, and a similar effect which occurs when the diffused light emerges from the water, make it possible to detect an appreciable dependence on the azimuth of observation of the colour, even without the use of the observing nicol.

† Much in the same way as the polarisation of sky-light, even at 90° from the sun, is incomplete. It is also possible that the imperfectness of the polarisation of the molecularly-scattered light (due to asymmetry of the molecules or other cause) may contribute to this result. But on this point, the author reserves opinion.

colour of the sea, as observed with the aid of a nicol when the sky is completely overcast by clouds, also appears of a distinctly deeper tint than sunlit water. It is probable that this may, at least in part, be due to the importance of multiple scattering in such cases.

The difference between the colour of the parts of a wave sloping towards and away from the observer has already been mentioned and explained. A remarkable feature noticed in this connection is that when the surface of the sea is viewed through a nicol, the degree of contrast varies enormously as the nicol is rotated about its axis. The precise effect, of course, depends upon the relative intensity, colour, and polarisation of the light reflected from the surface of the water at different angles and of the light emerging from inside the water. Broadly speaking, the phenomenon observed is that in one position of the nicol the sea appears almost flat and undisturbed, and in another position ruffled and full of ripples. The visibility of the horizon, which depends on the contrast between sea and sky, also varies, in some cases very greatly, as the nicol is rotated.

9. *Colours of the Transmitted Light.*

Finally, a few remarks would not be out of place regarding the nature of the colours observed when an opaque body, *e.g.*, a white plate, is immersed at some depth under water. It should not be assumed that the colour which it exhibits really corresponds to that transmitted by an equivalent column of water of twice the depth. The observed effect is really the resultant of two distinct factors: (*a*) the light molecularly scattered upwards towards the observer by the column of water between the plate and the surface; and (*b*) the light scattered by the plate and reaching the observer after attenuation in passing through the column of water. The effect (*b*) itself is composite, for the light reaching the plate and scattered by it consists of two parts: (*c*) regularly transmitted light, and (*d*) lateral illumination of the plate, due to molecular scattering in the liquid. It is clear from this that the colour of the plate would appear much bluer than that of the transmitted light really is, and that observations of the latter by this method are quite futile.

10. *Summary and Conclusion.*

The paper puts forward a new theory of the colour of the sea, namely, that it is due to the molecular scattering of light in water. The following are the principal conclusions contained in the paper:—

(*a*) The intensity of molecular scattering in water can be calculated from the "theory of fluctuations" developed by Einstein and Smoluchowski, and is

found to be in round numbers 160 times that in dust-free air.   This agrees
with the value observed experimentally.

(b) The coefficient of extinction of light in water calculated from theory
also agrees with the observed value in the parts of the spectrum in which
there is no selective absorption.

(c) A sufficiently deep layer of pure water exhibits by molecular scattering
a deep blue colour more saturated than sky-light and of comparable intensity.
The colour is primarily due to diffraction, the absorption only making it of a
fuller hue.

(d) The theories hitherto advanced that the dark blue of the deep sea is
reflected sky-light or that it is due to suspended matter are discussed and
shown to be erroneous.

(e) A number of interesting effects, due to polarisation and multiple scat-
tering observed at sea, are described and explained.

(f) It is pointed out that the colour of a white plate as seen when
immersed at some depth under transparent water does not really correspond
to the character of the transmitted light.

The author is indebted to Mr. L. A. Ramdas, post-graduate scholar, for
efficient assistance in the experimental work.

The Design of Repeating Patterns.—Part I.

By Major P. A. MacMahon, F.R.S., and W. P. D. MacMahon, F.R.A.S.

1. By a repeating pattern, or "repeat," as it is sometimes termed for brevity
of expression, is to be understood a figure in two dimensions of such shape
that a number of figures identical with it may be assembled so as to fill space
of two dimensions without leaving any interstices.   We include in the definition
any number of separate figures, relatively fixed in position, which, as a whole,
possess the repeat property.

The object of the present communication is, after some general notions
concerning the subject, to establish a simple method for the design of repeats
which leads naturally to a useful classification of these geometrical forms.
In particular, in view of the circumstance that it is æsthetically desirable to
construct forms which possess some kind of symmetry, a calculus for the design
of symmetrical repeats is brought forward.[*]

[*] The subject studied herein has been broached in a little book by the first author,
entitled 'New Mathematical Pastimes,' which is on the point of publication by the

2. The geometry which is involved is of a novel but simple character. It is entirely two-dimensional so long as patterns in two dimensions are in view. Two figures are looked upon as identical only when they can be made to coincide by movements in the plane. If two figures be such that one is the image of the other, but not identical with it, and one be denoted by a, the other is conveniently denoted by Ia, and, when necessary, the position of the line which determines the position of the image will be stated.

If a point α be joined to a fixed point O in the plane and the line αO be produced an equal distance to α'; α, α', are the point images of one another (or are in point symmetry) with respect to the point O.

Any locus of points α has a point image with respect to O which is the locus of the corresponding points α'.

The point image of a figure with respect to any point in its plane is an identical figure rotated through two right angles about an axis perpendicular to the plane.

The figure and the point image are conveniently denoted by

$$a, \ \mathrm{P}a,$$

the point O being specified when it is necessary to fix the relative positions of the two figures.

Generalities concerning Repeats.

3. It is convenient to bring together some well known facts, along with others which may not be well known or may be new.

The only regular polygons which are repeats are the equilateral triangle, the square, and the regular hexagon.

These are important bases for use in the method of construction which will be presented.

Every parallelogram is a repeat.

Since any parallelogram can be divided into two identical triangles by drawing either diagonal, it follows that

Every triangle is a repeat.

4. *Every Quadrilateral is a Repeat.*

This valuable result appears hitherto to have escaped the notice of geometricians.† It is fundamental in the subject, and is obvious to any geometrician almost as soon as it is stated. It follows readily from the fact that the sum of the interior angles is equal to four right angles.

Every hexagon in which each pair of opposite sides involves lines which

Cambridge University Press. It is there dealt with as affording a mathematical recreation, and is not seriously considered from a scientific point of view.

† The result for a *convex* quadrilateral is given as Example 14, p. 86, of Sommerville's 'Non-Euclidean Geometry,' 1914.

are equal and parallel is a repeat. This theorem is obvious directly a few hexagons are assembled. In this case the sum of three alternate interior angles is equal to four right angles.

Observe also that if we join two opposite angular points of such a hexagon, we divide it into two identical quadrilaterals, and that any quadrilateral is obtainable in this way. Since the hexagon is a repeat, its bisection into identical quadrilaterals establishes the quadrilateral as a repeat. Conversely, if we assume the repeat property of the quadrilateral, that of the hexagon is established.

5. *The Principle of Dissection.*

We have found that the parallelogram and the special hexagon above defined give each rise to a new repeat by bisection into identical figures. We have here a general principle. Whenever it is possible to dissect a repeat into a number of identical figures, the figure so derived is a repeat.

6. *The Principle of Composition.*

When we assemble a given repeat, we can in general draw a boundary enclosing two or more repeats, such that the figure enclosed by the boundary is a repeat. Thus, from the quadrilateral repeat we derive the special hexagon repeat. Many examples of composed repeats present themselves later. The principle is the converse of that of " dissection."

7. *Nature of an Assemblage of Repeats.*

When a repeat is assembled, it *may* always appear in the same orientation. Such is the case with the square, the regular hexagon, and the special hexagon connected with the quadrilaterals. Such an assemblage may be said to exhibit one aspect of repeat.

On another hand, if we assemble the equilateral triangle, the general quadrilateral and an infinite number of other repeats, we find that the assemblage exhibits two aspects of the repeat. Other assemblages, according to the nature of the repeat, involve three, four, or six aspects.

This is not the whole story, because some repeats can be assembled in more than one way, and these ways may exhibit different numbers of aspects. As an example, it will be shown that one category of repeats is such that every member of it may be assembled in three different ways, exhibiting one, two, and four aspects respectively. The nature of the assemblage in regard to aspect is an important feature of the classification. At the present stage it need only be remarked that the equilateral triangle is the only one of the three repeating regular polygons that *cannot* have fewer than two aspects in assemblage. In general, a repeat derived by " dissection " has more aspects when assembled than the repeat dissected ; and, conversely, the repeat derived by " composition " has fewer aspects than the repeat from which it is derived.

8. *The Principle of Absorption.*

To explain, we make an assemblage of equilateral triangles, a tessellation, and number the triangles, which have the same aspect, 1, and the remaining triangles are numbered 2. Then we see that every triangle numbered 1 or 2 is adjacent to three triangles numbered 2 or 1 respectively. Dissect each of the triangles numbered 2 by lines drawn from the centre to the vertices. Add to the triangles numbered 1 the adjacent thirds of each of the adjacent triangles; thus forming an assemblage of regular hexagons at the expense of the triangles numbered 2, which have all been absorbed by the triangles numbered 1.

This is the simplest illustration of the principle. It may be at once generalised for the equilateral triangle by taking any trisection at pleasure into three identical figures. The square, the regular hexagon, and many other simple forms may be treated in a similar manner.

9. *The Principle of Line Transformation.*

It is convenient to regard the equilateral triangle as the simplest repeat. The simplest way (not the only one) of assembling it is to cause each side to touch, throughout its entire length, the side of another triangle. The method of transformation, as applied to such an assemblage, consists in transforming each triangle to some other shape, the same in each case, so that the flat space is still filled up without leaving interstices. When this is carried out the triangle, as transformed in shape, is established as a repeat.

To effect such a transformation we divide the triangle into three compartments by straight lines drawn from the geometrical centre to the vertices, and suppose the three identical compartments to be numbered 1, 2, 3, such numbers being in ascending order of magnitude when read counter-clockwise about the centre. It is convenient to regard these numbers as symbolising colours.

It is not quite a trivial remark that these triangles may be assembled so that the colours 1, 2, 3 are adjacent to the colours 1, 2, 3 respectively. The fact is established by the diagram, fig. I, which may be extended indefinitely.

If the colours 1, 2, 3 be the same we have the ordinary tessellation composed of identical equilateral triangles; we have nothing new. But if the colours be not the same we have an assemblage subject to a certain *contact system* which may be briefly denoted by

1 to 1, 2 to 2, 3 to 3, or 11, 22, 33.

We have a *new kind of repeat.*

10. Moreover the contact system may be varied.   In the present instance there is only one other essential variation, viz., the contact system

<p style="text-align:center">1 to 1, 2 to 3,   or   11, 23.</p>

This is established by the diagram, fig. II, which can be extended indefinitely.   We have again a new repeat because the assemblage is subject to another system of contact.   The diagrams show that the new repeats exhibit two and six aspects respectively.

There may be identities between the colours which must be subjected to examination, but *always* the contacts are of two, and only two, natures :—

(i) The adjacent compartments are similarly coloured.

(ii)   „   „   „   differently   „

11. We next seek to distinguish the three compartments of the triangle, not by different colours, but by altering the shapes of the compartments differently.   The object is to abolish the colours by transforming the colours into shapes.

The First Nature of Contact.

The adjacent compartments are similarly coloured.

In the left-hand diagram of fig. III, the common boundary of the compartments coloured 1 is a straight line; in the right-hand diagram the colour 1 has disappeared and the adjacent compartments have a common zig-zag boundary which is of such a shape that the two triangles have been transformed so that they remain of the same shape.

We have thus a repeat of a new shape and involving two colours.   The assemblage is subject to the contact system

<p style="text-align:center">22, 33.</p>

The enquiry is now into the law which controls the shape which replaces the colour.

If AB be the initial boundary we see that the new boundary line which connects the points AB must not be changed in orientation by a rotation through two right angles about a perpendicular, through the mid-point of AB, to the plane of the paper.   In other words the point image of the new boundary with respect to the mid-point of AB must be identical with that boundary both in shape and orientation.

If we desired to treat each of the three colours in the same way, we could restrict the new boundary so as to lie entirely within the rhombus originally formed by the two compartments, coloured 1, when in contact.   But this is not always to be desired, and other bases than the equilateral triangle come into view, and other conditions.   The principles which will now be set forth

are applicable to all bases and to various conditions, so that it is not convenient to restrict in any way the delineations of boundaries which explain and exemplify the principles, but rather to leave them to be subsequently modified so as to conform to requirements which may present themselves.

Suppose that the dotted line AB denotes the original boundary of the compartment coloured 1 and that the base piece extends below AB, the shape of the piece and of the compartment not being at present before us.

Change the boundary to the zig-zag $AbOaB$ where O is the mid-point of AB. If $AbOaB$ be its own point image with regard to O it follows that the part BaO above AB is the point image of the part AbO below AB, fig. IV.

In general we can draw any system of closed curves above AB and the corresponding closed curves, point images of the former, below AB and the required transformation will be effected.

The closed curves above AB determine additions to the base piece while those below AB determine corresponding pieces which must be cut away from the base. Examples are given in fig. XV.

Shapes thus defined fit together and are to be employed in substitution of the colour. Each colour is treated on the same principle but care must be taken that the several transformations are compatible with one another. More upon the subject of compatibility is postponed to a later stage in the paper.

12. *Symmetry of Shape.*

Having a symmetrical calculus in view we must distinguish between the transformation patterns which are symmetrical about the line which bisects the line AB at right angles and those which do not possess this symmetry.

The symmetrical shape will be denoted by

$$S_1$$

the unit suffix denoting that the first nature of contact (that between identical colours) is in view.

Different symmetrical shapes are denoted by

$$S_1, \quad S_1{}', \quad S_1{}'', \dots.$$

The unsymmetrical shapes are denoted by

$$U_1, \quad U_1{}', \quad U_1{}'', \dots.$$

It must be noticed that the symmetrical shape has the same shape as its image with respect to a line perpendicular to AB in the plane of the paper so that

$$S_1 \equiv IS_1$$

but
$$U_1 \not\equiv IU_1.$$

The symbol I is not to be regarded as an operator. The notation merely means that the patterns U_1, IU_1 are related to one another in a certain manner.

Briefly to resume, we may say that, denoting the base figure by a shaded area, we may take any system of shaded areas exterior to and above AB (additions to the base) and a corresponding system of unshaded areas within the area of the base figure (gaps in the base piece), the boundaries of the shaded and unshaded areas being point images of one another with respect to the mid-point of AB.

On the suggestion of Mr. G. T. Bennett we call repeats which have gaps in them "stencil" repeats, and those which involve several separate pieces, relatively fixed in position, "archipelago" repeats. Both of these come into view in the transformation due to the first nature of contact.

13. *The Second Nature of Contact.*

Here a colour 2 is invariably adjacent to a colour 3. We require a transformation such that it is mechanically impossible for the compartments so coloured to be in juxtaposition in any other manner.

It is clear that if we take, in respect of the compartment coloured 2, any system of closed curves above AB and any system below AB within the base as a definition of its transformation we at the same time completely determine the transformation pattern that must be associated with the colour 3.

We always view the transformation pattern from the inside of the base looking outwards, so that the closed curves which define the shape associated with the colour 3 are derived from those which define the shape associated with the colour 2, by taking the point image of the latter with regard to the mid-point of AB, fig. V.

Suppose then that we are given, by shaded and unshaded areas, the transformation pattern of the colour 2, we take the point images of the contours of the added and subtracted areas with respect to the mid-point of AB, shading those areas which then become exterior to the base, and leaving unshaded those which become interior.

We thus arrive at the transformation pattern for the colour 3. Examples will be seen in fig. V.

The two transformation patterns are connected in the same way as the exterior and interior patterns arising from the first nature of contact. The first nature of contact can, in fact, be exhibited as two contacts of the second nature, one on each of two halves of the original boundary.

The only condition of transformation is that the two transformation patterns, determined as above, must be *different*. In the contrary case they would belong to the first nature of contact.

Put in another way, we have merely to take any convenient set of closed curves, not belonging to the first nature of contact, to replace the colour 2; and then the point image process produces the closed curves which are to be taken to replace the colour 3. Examples are shown in fig. XV.

14. For the purpose of the symmetrical calculus these patterns are separable into three classes:—

(i) Those which are symmetrical about a straight line at right angles to AB and passing through its mid point.

Such will be denoted by

$$S_2, \quad S_2', \quad S_2'', \dots .$$

(ii) Those which do not belong to the class (i), and, further, are not symmetrical about AB. Such will be denoted by

$$U_2, \quad U_2', \quad U_2'', \dots .$$

(iii) Those which do not belong to the class (i) but are symmetrical about AB. Such will be denoted by

$$V_2, \quad V_2', \quad V_2'', \dots .$$

the suffix 2 always denoting that the second kind of contact is in view.

Examples of the three classes are given in fig. XV.

16. The symbol I being as defined above

$$IS_2 \equiv S_2, \quad IU_2 \not\equiv U_2, \quad IV_2 \not\equiv V_2.$$

For a 2 to 3 contact, if S_2, U_2, V_2, be patterns associated with the colour 1, PS_2, PU_2, PV_2, denote the patterns to be associated with the colour 2.

In the shapes, symbolised by V_2,

$$PV_2 \equiv IV_2.$$

15. *The Construction of Symmetrical Repeats.*

A repeat may be symmetrical—

(i) About an axis in the plane of the paper.

(ii) By being unchanged by certain rotations about an axis perpendicular to the plane of the paper.

In the case of (i) there are definite principles which it is useful to recognise at once.

The axis of symmetry will usually be either a straight line passing through an angular point of the base polygon or a straight line which is perpendicular to a side of the base polygon, at the mid-point of the side.

Suppose that AB, A'B' are two equal sides of the base polygon, and symmetrically situated with regard to the axis $\alpha\beta$.
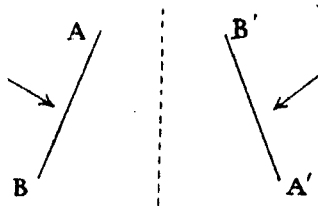

The boundary patterns are viewed in the direction indicated by the arrows. We obtain symmetry by taking

for AB S_1,   for A'B' S_1,

,, U_1,   ,, IU_1,

,, S_2,   ,, S_2,

,, U_2,   ,, IU_2,

,, V_2,   ., $PV_2 \equiv IV_2$.

In the case of (ii) there is no difficulty in obtaining symmetry. The matter will be dealt with when the various bases are brought into view.

16. We are now in a position to resume the discussion of the repeats which may be derived from an equilateral triangular base. It is, as above remarked, essential to secure compatibility between the transformation patterns. If we take any point O in the area of the triangle (fig. VI) and join it to the vertices, we divide it into three parts which may be associated with the corresponding sides, BC, CA, AB. We may take the triangles OBC, OCA, OAB for the coloured compartments. The point image of O with respect to the mid-points of the three sides being the points A', B', C', we may take the parallelograms OA', OB' OC' for the areas within which the transformation patterns are to be restricted, where the contact system only involves contacts of the first nature. (Readers will supply letters to fig. VI.)

To obtain a generalisation, observe that we may proceed in a similar manner in regard to *any* division of the triangle into three parts. In particular, we may associate the parallelograms OA', OB', OC', above, in any manner with the sides, BC, CA, AB. Since the triangular base has symmetry of the third order, the number of different shapes thus obtained from the same division of the triangle and the same transformations will be two, viz., the number of permutations of three different things arranged in circular order. If the base is without symmetry, there will be the full number, six, of different repeats derived from the same division of the triangle and the same transformations.
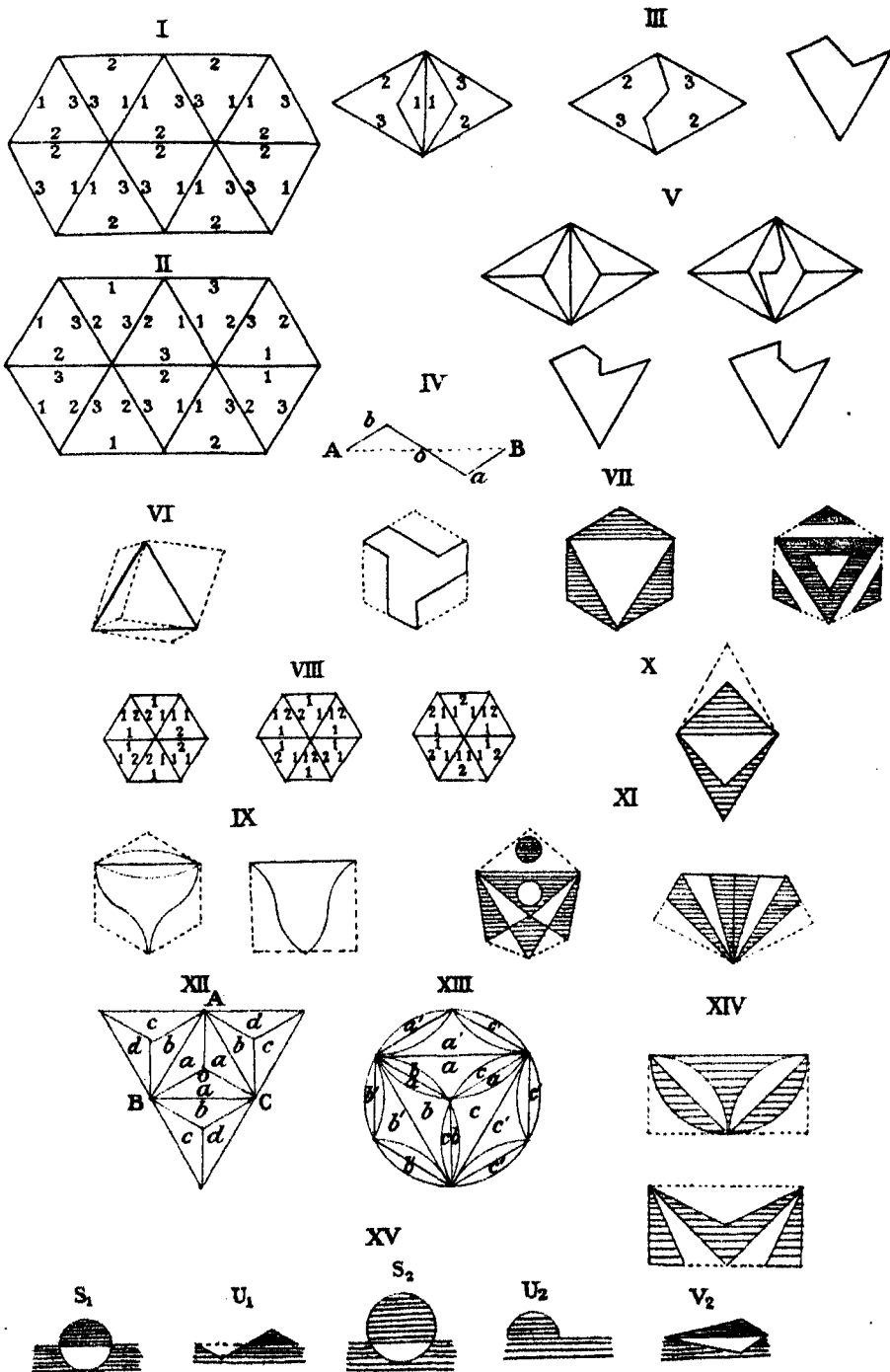
17. *The First System of Contact.*

There are three cases to consider corresponding to the colouring of the compartments in the ways

$$(a)\ 1, 1, 1, \qquad (b)\ 1, 1, 2, \qquad (c)\ 1, 2, 3.$$

In order to exhibit some of the results, we may take the simplest trisection of the triangle to guide the transformations. For (a) three examples are given in fig. VII. They are examples of " block," " stencil," and "archipelago " repeats respectively.

18. The stencil example is of particular interest because it can be used as an actual stencil to produce the equilateral triangle repeat which is the base of the system. This observation may appear at first sight to be trivial but in reality supplies the first glimpse of a principle of great importance. It is in general possible to draw a contour surrounding any given repeat in such wise that the area inside the contour, which is not part of the original repeat, itself is a repeat. In the present instance the contour referred to is a regular hexagon and the illustration by its shaded and unshaded portions exhibits two repeats.

The duality arises in the following way. If in a rhombus, to which the pattern which replaces the colour is restricted, we draw the system of closed curves according to rule, it is clear that those areas of the rhombus which have not been enclosed possess the same property, viz., the boundaries of those areas which are inside the boundary of the base are the point images of those which are outside that boundary. It follows that the boundary patterns which replace the colours always present themselves, *quâ* the rhombus, in pairs. Moreover, for *any* division of the triangle base into parts and for *any* association of these parts with the sides of the triangle, the transformation patterns invariably present themselves in pairs.

It will be observed also that the external boundary, in the present instances a regular hexagon, also by itself determines a repeat so that in reality each figure exhibits three repeats. In connection with this circumstance there is a theory of some elegance which will be dealt with later in the paper. It is involved in one of the fundamental theorems of the geometry of repeats.

The repeats of this category, viz., 1, 1, 1, can be assembled in only one manner and two aspects are always exhibited. The category embraces an infinite number of repeats.

19. For *b* (1, 1, 2) there are three ways of assembling exhibiting 6, 2, 6 aspects of the repeat respectively, fig. VIII.

In the transformation of the colours 1, 2 we select any two of the patterns symbolised by S_1, U_1 and we may take for the point O which determines the areas within which the patterns may be drawn, any point in the area of the

triangle. An example of repeats of this category is shown in fig. X the external boundary which determines a second repeat being shown dotted.

20. For c (1, 2, 3) we select three different patterns and by using both U_1 and IU_1 it is easy to secure symmetry. Examples are given in fig. IX.

21. *The Second System of Contact,* 1 to 1, 2 to 3 or 11, 23.

There is only one way of constructing a symmetrical repeat, viz., by taking S_1 for 1, V_2 for 2, and PV_2 for 3.

Take the point O upon a perpendicular and join it by straight lines to the other two vertices. The perpendicular being the axis of symmetry the compartments coloured 2, 3 are on either side of it and it bisects the compartment coloured 1. Construct the images of the compartments coloured 2, 3 in the corresponding sides and the point image (in the present instance this is the same as the image) of that coloured 1, thus forming an exterior polygon, viz., a hexagon. It is clear that if we construct any V_2 pattern within the prescribed area the portion of that area which does not belong to the pattern will also be a V_2 pattern. Hence the exterior polygon may be employed to form a second repeat by the process of cutting away from it any repeating pattern which has been constructed according to rule. In particular we may cut away the triangular base.

We may also vary the trisection of the triangle in the manner described in Nos. 5, 22, and proceed to an external contour by taking two images and one point image as above. Examples are shown in figs. X, XI.

22. *Concerning the Principles of Dissection and Composition.*

There is a point that is made conveniently at this stage of the research. The equilateral triangle yields an infinite number of repeats by trisection into three identical parts, the lines of section being straight or curved and drawn through the geometrical centre.

Conversely any one of these repeats may be assembled so as to form other repeats. Now the three identical pieces into which the triangle has been dissected may be put together so as to form a repeat in *more than one way.* Thus looking at the diagram, fig. XII, the repeat marked a may be assembled as to form the original equilateral triangle. If we take the point images of the repeats thus placed with regard to the mid-points of the adjacent sides, we obtain the stencil repeat constituted by the areas marked b. Further, if we take the point images of the areas AoA, BoC, CoA, with regard to the mid-points of CA, AB, BC, respectively, we arrive at the archipelago repeat constituted by the areas marked c; and if with regard to the mid-points of BC, CA, AB, respectively, the archipelago repeat constituted by the areas marked d. We can, therefore, in every case assemble the repeat in four different ways so as to form another repeat. The proof of the above follows at

once from the rules of transformation that have been given. This point will appear again at a later stage.

23. *The Classification of Repeats.*

The foregoing pages suggest a method of classifying repeats depending upon :

(1) the simple geometrical form taken as base ;

(2) the contact system which guides the transformation from colour to shape ;

(3) the nature of the colouring of the compartments of the base ;

(4) In the case of symmetrical repeats the transformation is indicated by the symbols S_1, U_1, S_2, U_2, V_2.

We will denote the equilateral triangle base by the letters T. E. and the contact systems 11, 22, 33 ; 11, 23 by (i), (ii), respectively, so that the classification is

T.E.   (i) 1, 1, 1 ;   1, 1, 2 ;   1, 2, 3.

T.E.   (ii) 1, 2, 3.

For symmetrical forms we have the five categories :—
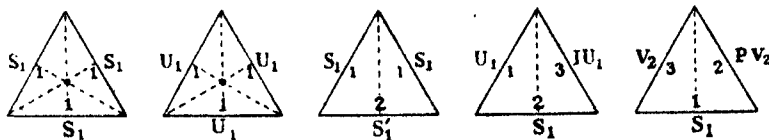
24. *The Theory of Complementary Repeats.*

It is evident from the preceding discussion that every repeat is associated with an infinite number of complementary repeats which are determined by the division of the base into three (n) portions. One or both (some or all) of two ($n-1$) of the portions may have no area and therefore be non-existent.

On the other hand the dissection of the triangle (base polygon) may be into any number of distinct areas, and these may be grouped into three (n) lots, constituting the three (n) portions ; moreover, any number up to two ($n-1$) of these lots may be non-existent.

To illustrate this point consider the circular stencil repeat derived from the equilateral triangle, fig. XIII. The division of the triangle is into nine areas grouped into three lots marked a, b, c, respectively. The point images of these with respect to the corrresponding sides are marked a', b', c', respectively. In regard to the upper side the areas marked a and a' are available for the transformation pattern of type S_1, and similarly for the other sides the areas marked b, b' ; c, c'.

The pattern of the repeat is given by the *small* areas a', b', c', and the large areas a, b, c.

The exterior contour which determines the complementary repeat is composed of the boundary lines of the small areas a', b', c', and the *curved* boundaries of the larger areas a', b', c'. The contour consequently consists of seven distinct closed boundaries of which six enclose the small areas a', b', c'.

The complementary repeat is constituted by the collection of areas enclosed by the seven contours which do not belong to the first repeat. There are no such areas enclosed by the six small contours, so that *effectively* the exterior contour is determined by the curved boundary of the large areas a', b', c', and we are led to the complementary repeat constituted by the *large* areas a', b', c' and the *small* areas a, b, c.

It may be noted also that the third repeat (see fig. XIII) consists of the whole of the areas marked with the letters a, b, c, a', b', c', and is identical with the circular repeat that is derivable from a regular hexagonal base. This is a stencil form and is the nearest approach to a circular block repeat that it is possible to construct.

The subject of complementary repeats in general is considered again in Part II.

25. *The Isosceles Right-Angled Triangle Base T. R.*

We can divide the triangle into three parts in any manner, but for present purposes it is convenient to effect the division by joining the vertices to some point O upon the perpendicular drawn from the right angle on to the base. For most purposes it suffices to take the point O at the centre of gravity of the triangle. We number the compartments 1, 2, 3 in counter-clock-wise order and first consider the contact system

$$11, \quad 22, \quad 33.$$

Assemblage can be made in one way; but when the colours 2, 3 are identical a second way of assembling is found which exhibits four aspects instead of two.

With the contact system

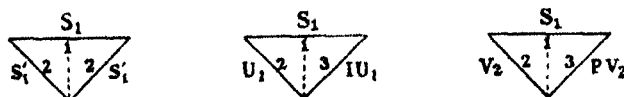$$11, \quad 23,$$

there is only one way of assembling and this exhibits four aspects. The classification is

T.R.   (i) 1, 2, 2;   1, 2, 3.

T.R.   (ii) 1, 2, 3.

There are three symmetrical repeats :—

Some examples are given in fig. XIV.

The point O which determines the dissection of the base is conveniently taken either at the middle point of the hypothenuse or at the centre of gravity. The exterior boundary which determines a second repeat is shown in dotted lines.

26. The isosceles triangle with vertical angle 120°, T. $\frac{2}{3}\pi$ can be assembled either on the contact system 11, 22, 33, or on 11, 23.

The classification is

$$\text{T. } \tfrac{2}{3}\pi. \quad \text{(i) } 1, 2, 2; \quad 1, 2, 3.$$
$$\text{T. } \tfrac{2}{3}\pi. \quad \text{(ii) } 1, 2, 3.$$

There are three symmetrical repeats :—
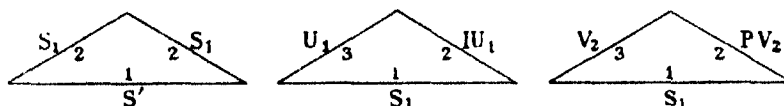
The point O may be suitably placed either at the vertex or at the mid point of the long side.

Correlation between Arrays in a Table of Correlations.

By C. SPEARMAN.

Two recent papers in these Proceedings have dealt with certain problems of probability which are of very great importance for psychology in particular, but in themselves are quite general.[*]   As both papers made reference to some of my own, the following considerations may not only be a further positive contribution to the topic, but incidentally serve to clear up some misunderstandings.

Suppose that the product moment coefficients of correlation have been determined between any set of variables $a, b, c, d, \ldots z$, and have been set forth in a square Table thus :—

	a	b	c	.	.	z
a		r_{ab}	r_{ac}	.	.	r_{az}
b	r_{ab}		r_{bc}	.	.	r_{bz}
c	r_{ac}	r_{bc}		.	.	r_{cz}
.	.	.	.	.	.	.
.	.	.	.	.	.	.
z	r_{az}	r_{bz}	r_{cz}	.	.	

[*] Maxwell Garnett, 1919 ; G. Thomson, 1919.

Both the said papers dealt with the problem as to how the correlation between parallel arrays of these coefficients (ignoring the coefficient that has no partner) are related to the inner constitution of the variable. One of the papers (Garnett) further inquired as to how this inner constitution is related to the general satisfaction of the equation,

$$r_{xy} = \lambda_{xz} r_{yz}, \text{ where } \lambda_{xz} \text{ is constant whilst } y \text{ takes all values}$$
$$\text{except } x \text{ or } z.^{*} \tag{1}$$

The present paper will endeavour to provide a general method for solving many of the cases at issue, and also will attempt actually to solve certain cases of primary importance.

1. Following Bravais (and also Pearson), we will represent each of the variables as a function of a number of elements uncorrelated with one another.

$$\left. \begin{array}{l} a = \phi\,(\epsilon_1\epsilon_2 \ldots \epsilon_\kappa\,\epsilon_{\kappa+1} \ldots \epsilon_\nu) \\ b = \psi\,(\epsilon_1\epsilon_2 \ldots \epsilon_\kappa\,\epsilon_{\nu+1} \ldots \epsilon_\mu) \end{array} \right\} \tag{2}$$

where $\epsilon_1 \ldots \epsilon_\kappa$ are the elements common to both functions, whilst the rest occur only in one.

If, then, a and b are taken to have been measured respectively from their means as origins, and if—again with both Bravais and Pearson—we assume that these two functions are represented with sufficient approximation by Taylor's expansion to the first differentials, we get

$$a = A_1\epsilon_1 + A_2\epsilon_2 + \ldots A_\nu\epsilon_\nu, \text{ and similarly for } b, c, \ldots z. \tag{3}$$

For convenience, this may be written as $a = \overset{r=\omega}{\underset{r=1}{\Sigma}} (A_r\epsilon_r)$, where the Σ indicates summation over all the elements entering into *any* of the variables $a, b, \ldots z$, the coefficient A being taken as zero whenever the element is not present really.

Then, in the case of any particular observation of the variable a, say the mth, we get

$$a_m = \overset{r=\omega}{\underset{r=1}{\Sigma}} (A_r,\, \epsilon_{mr}), \tag{4}$$

and, letting S indicate summation with respect to the different observations of the same variable, we may for further convenience

denote $\qquad\qquad A_r^2 \cdot \overset{m=n}{\underset{m=1}{S}} (\epsilon_{mr}^2) \text{ by } A_r'^2.$ $\qquad\qquad$ (5)

---

* Otherwise expressed as $r_{px}/r_{qx} = r_{py}/r_{qy}$ for the psychological significance of which, see Spearman, 'Psychological Review,' vol. 27, p. 159.

Hereupon, bearing in mind that by hypothesis all products vanish,

$$\underset{m=1}{\overset{m=n}{S}} (a_m{}^2) = \underset{\tau=1}{\overset{\tau=\omega}{\Sigma}} [A_\tau{}^2 . \underset{m=1}{\overset{m=n}{S}} (\epsilon_{m\tau}{}^2)] = \underset{\tau=1}{\overset{\tau=\omega}{\Sigma}} [A_\tau{}'^2], \text{ and similarly}$$

$$\underset{m=1}{\overset{m=n}{S}} (b_m{}^2) = \underset{\tau=1}{\overset{\tau=\omega}{\Sigma}} [B_\tau{}'^2]$$

$$\underset{m=1}{\overset{m=n}{S}} (a_m b_m) = \underset{\tau=1}{\overset{\tau=\omega}{\Sigma}} [A_\tau' B_\tau'] \qquad (6)$$

Writing next $A' \Big/ \sqrt{\left(\underset{\tau=1}{\overset{\tau=\omega}{\Sigma}} [A_\tau{}'^2] \right)}$ as A'', and similarly B'', (7)

we get $$r_{ab} = \underset{\tau=1}{\overset{\tau=\omega}{\Sigma}} [A'' B'']. \qquad (8)$$

In similar fashion, the correlations of a and b with the rest of the variables $c \ldots z$ can be arranged in two columns as follows (dropping, for brevity, the indices to the symbols of summation)

$$
\begin{aligned}
r_{ac} &= \Sigma [A''C''], & r_{bc} &= \Sigma [B''C''] \\
r_{ad} &= \Sigma [A''D''], & r_{bd} &= \Sigma [B''D''] \\
& \cdot \quad \cdot \quad \cdot & & \cdot \quad \cdot \quad \cdot \\
r_{az} &= \Sigma [A''Z''], & r_{bz} &= \Sigma [B''Z'']
\end{aligned}
\qquad (9)
$$

If, next, R_{ab} denotes the coefficient of correlation between the two columns and x is any of the variable $c, d \ldots z$, then

$$R_{ab} = r_{\Sigma[A''X''] . \Sigma[B''X'']} = r_{\Sigma[A'X''] . \Sigma[B'X'']},$$

since the factors $\sqrt{(\Sigma [A'^2])}$ and $\sqrt{(\Sigma [B'^2])}$ are constant and positive.

Hence, expanding by the formula for correlations of sums,[*] and using again Σ to denote summation in respect of all the elements from ϵ_1 to $\epsilon_{\omega 1}$, whilst σ and n refer to χ taking successively the values $C, D \ldots Z,$

$$R_{ab} = \frac{\underset{\beta}{\Sigma} [A_\beta' B_\beta' \sigma_{x_\beta''}{}^2] + \underset{\beta \neq \gamma}{\Sigma} [A_\beta' B_\gamma' \sigma_{x_\beta''} \sigma_{x_\gamma''} r_{x_\beta'' x_\gamma''}]}{\sqrt{(\underset{\beta}{\Sigma}[A'^2 \sigma_{x_\beta''}] + 2 \underset{\beta \neq \gamma}{\Sigma} [A_\beta' A_\gamma' \sigma_{x_\beta''} \sigma_{x_\gamma''} r_{x_\beta'' x_\gamma''}])}} . \qquad (10)$$
$$\sqrt{(\underset{\beta}{\Sigma}[B_\beta'^2 \sigma_{x_\beta''}{}^2] + 2 \underset{\beta \neq \gamma}{\Sigma} [B_\beta' B_\gamma' \sigma_{x_\beta''} \sigma_{x_\gamma''} r_{x_\beta'' x_\gamma''}])}$$

2. Now, this last equation (10) has numerous applications and simplifications according to any special conditions that may be introduced. We will here apply it to the most important condition of all, that is, where all the correlations derive from one and the same element alone, *e.g.*,

$$a = A_1 \epsilon_1 + A_\nu \epsilon_\nu + \ldots$$
$$b = B_1 \epsilon_1 + B_\mu \epsilon_\mu + \ldots$$
$$\cdot \quad \cdot \quad \cdot$$
$$z = Z_1 \epsilon_1 + Z_\theta \epsilon + \ldots$$

$\epsilon_\nu, \epsilon_\mu,$ and $\epsilon_\theta,$ etc., being always different.

[*] Spearman, 'Brit. J. Psych.,' vol. 5, p. 419 (1913).

Then, no summation with respect to τ is required for (8) and (9). For (10), the second term in the numerator, as well as under each of the roots in the denominator, vanishes. We have, therefore,

$$R_{ab} = \frac{A'B'\sigma_{x''}^2}{\sqrt{(A'^2\sigma_{x''}^2)}\sqrt{(B'^2\sigma_{x''}^2)}} = \pm 1, \qquad (11)$$

according as A' and B' are of the same or different signs. This is in agreement with the conclusions reached previously (by way of Udny Yule's formula for partial coefficients), that the present assumption of there being only one single common element leads to equation (1).*

In this connection, consider also the case where the variables $a, b, \ldots z$ have several common elements, but always the same and in similar proportions, $e.g.$,

$$p = \lambda_{pq}Q_\zeta\epsilon_\zeta + \ldots + \lambda_{pq}Q_\theta\epsilon_\theta + \ldots P_\rho\epsilon_\rho + \ldots + P_\xi\epsilon_\xi, \text{ where } \epsilon_\zeta \ldots \epsilon_\theta$$

are common to all the variables, whilst no others are common to any : λ_{pq} is constant for different elements. Then, since X_β is always in the same proportion to X_γ, so also is X_β'' to X_γ'' whereby $r_{x_\beta'' x_\gamma''} = 1$. Hence using (10)

$$R_{ab} =$$

$$\frac{\Sigma[A'B'\sigma_{x''}^2] + \underset{\beta \neq \gamma}{\Sigma}[A_\beta'B_\gamma'\sigma_{x_\beta''}\sigma_{x_\gamma''}]}{\sqrt{(\Sigma[A'^2\sigma_{x''}^2] + \underset{\beta \neq \gamma}{\Sigma}[A_\beta'A_\gamma'\sigma_{x_\beta''}\sigma_{x_\gamma''}])}\sqrt{(\Sigma[B'^2\sigma_{x''}^2] + \underset{\beta \neq \gamma}{\Sigma}[B_\beta'B_\gamma'\sigma_{x_\beta''}\sigma_{x_\gamma''}])}}$$

$$= \frac{\Sigma[A'\sigma_{x''}] \cdot \Sigma[B'\sigma_{x''}]}{\sqrt{(\{\Sigma[A'\sigma_{x''}]\}^2)}\sqrt{(\{\Sigma[B'\sigma_{x''}]\}^2)}} = \pm 1, \text{ as before.} \qquad (12)$$

3. So far, our inferences have been from the inward structure of the variables to the values in the correlational table. But even more important is the inverse direction of inference, especially when applied to the same condition as before. That is to say, having seen that the fact of only one independent element being common to two or more variables proves both $R_{xy} = 1$ and also equation (1), the question now arises as to whether either of these equations proves that there can be only one element.

As regards $R_{xy} = 1$, this question must be reserved for another occasion. But as regards equation (1) the answer can be shown here to be quite generally affirmative.

The question is tantamount to asking whether, on assuming (1), each of the variables can be reduced to the form

$$a = f_a\eta + \delta_a \qquad (13)$$

where   1. f_a, f_b, etc., are constant for all particular values of a, b, etc.

2. η is an element common to all the variables.

3. δ_a, δ_b, etc., are uncorrelated with η,

4. δ_a, δ_b, etc., are uncorrelated with each other.

* Hart and Spearman, 'Brit. J. Psych.,' vol. 5, p. 58 (1912).

Now, we can always write any of the variables, say a, so as to satisfy 1 and 2, giving to f_a and to η any values we please, so long as, and only so long as, $\delta_a = a - f_a\eta$.

But in order to fulfil the third condition, we must also have

$$0 = r_{(a-f_a\eta)\,(f_a\eta)} \text{ which is equivalent to } 0 = \sigma_a r_{a\eta} - f_a\sigma_\eta,{}^*$$

which $= r_{a\eta} - f_a$, if this time we choose the units so that $\sigma_a = \sigma_b = \ldots \sigma_\eta = 1$. Hence we can fulfil the third condition by, and only by, making $f_a = r_{a\eta}$.

In such manner, the first three conditions can be satisfied for any set of variables whatever. But there remains the fourth condition, which will be satisfied if, and only if, we also obtain

$0 = r_{\delta_a\delta_b} = r_{(a-f_a\eta)\,(b-f_b\eta)}$ and therefore

    $= r_{ab} - f_a r_{b\eta} - f_b r_{a\eta} + f_a f_b,\dagger$ which, on replacing the f's by their values from (13)

$$= r_{ab} - r_{a\eta}r_{b\eta}. \tag{14}$$

This is effected easily in the case where the set of variables entering into the table of coefficients is very large. For then we need only choose for η the value of $\displaystyle\mathop{\mathbf{S}}_{x=a}^{x=z}(x)$, where the summation is over the said large number of variables, and there is a change of unit so as to make $\sigma_\eta = 1$. For now we get

$$r_{a\eta} = \frac{\sqrt{(m)}\,\bar{r}_{ax'}}{\sqrt{(1+[m-1]\,\bar{r}_{x'x''})}},\dagger \text{ where } x' \neq x'' \text{ denote any of the variables}$$

          including a itself, whilst m is the number of these variables

$$= \frac{\bar{r}_{ax'}}{\sqrt{(\bar{r}_{x'x''})}} \text{ approximately, since } m \text{ is by assumption very large.}$$

Hence,
$$r_{a\eta}r_{b\eta} = \frac{\bar{r}_{ax'}\bar{r}_{bx'}}{\bar{r}_{x'x''}} \tag{15}$$

But by (1), $r_{ab} = \dfrac{r_{ax}r_{bx^*}}{r_{xx^*}} = \dfrac{\overline{r_{ax'}r_{bx^*}}}{\bar{r}_{x'x''}} = \dfrac{\bar{r}_{ax'}\bar{r}_{bx} + \sigma_{r_{ax}}\sigma_{r_{bx}}r_{r_{ax}r_{bx}}}{\bar{r}_{x'x''}}.$ (16)

Further, the numerator of $r_{r_{ax}r_{bx}}$ can be written as $\overline{(r_{ax} - \bar{r}_{ax})(r_{bx^*} - \bar{r}_{bx})}$, which, owing to the largeness of m, approximates to the value it would have if x and x^* took all values quite independently of each other. And this is zero.

Again owing to the largeness of m, $\bar{r}_{ax'}$ and $\bar{r}_{bx'}$ approximate respectively to $\bar{r}_{ax}$ and $\bar{r}_{bx}$.

* Spearman, ' Brit. J. Psych.,' vol. 5, p. 419.
† See preceding footnote.

Accordingly, r_{ab} approximates to $\dfrac{\bar{r}_{ax'} \cdot \bar{r}_{bx'}}{\bar{r}_{x'x''}}$, which by (15) $= r_{a\eta}r_{b\eta}$, so

that $r_{\delta_a\delta_b} = 0$ and condition 4 is fulfilled as required. (17)

This not only corroborates the result obtained in the above mentioned paper of Garnett, but dispenses with his particular and precarious assumption of "normal" frequency distributions, so that it extends the theorem to one of perfect generality, except that m must be very large.

In order to fulfil condition 4, freed even from *this* limitation, the constitution of η must be more complicated. Let us choose for it the value expressed in the following determinant

$$
\begin{vmatrix}
p\sqrt{(S/M_i i)} & p\mu_a a & p\mu_b b & . & p\mu_z z \\
-1 & \mu_a{}^2-1 & 0 & . & 0 \\
-1 & 0 & \mu_b{}^2-1 & . & 0 \\
. & . & . & . & . \\
-1 & 0 & 0 & . & \mu_z{}^2-1
\end{vmatrix}
$$

where $\mu_a \equiv 1/\sqrt{(\lambda_{aq}r_{aq})}$, λ having a meaning as in (1), so that μ_a retains the same value whatever variable may be taken as q,

$i \equiv$ *any new* variable uncorrelated with all the others $(\sigma = 1)$,[*]

$M_i \equiv$ the complementary minor of the first element[†] in the first row,

$S \equiv$ the sum of such minors for all elements in the first row,

and p is such a value as will make $\sigma_\eta = 1$.

This gives us, expanding the determinant according to the elements of the first row,[‡]

$$
r_{a\eta} = \frac{\mu_a M_a + \mu_b M_b r_{ab} + \ldots + \mu_z M_z r_{az}}{\sqrt{(\mu_a{}^2 M_a{}^2 + \ldots + \mu_z{}^2 M_z{}^2 + M_i S + 2 S_x S_y [\mu_x \mu_y M_x M_y r_{xy}])}}.
$$

But by (1)

$$
r_{xy} = \lambda_{xq}r_{yq} = \lambda_{yq}r_{xq} = \sqrt{(\lambda_{xq}r_{xq})}\sqrt{(\lambda_{yq}r_{yq})} = 1/\mu_x \, 1/\mu_y, \text{ so that}
$$

$$
r_{a\eta} = \frac{1}{\mu_a} \frac{(\mu_a{}^2-1)M_a + S'}{\sqrt{([\mu_a{}^2-1]M_a{}^2 + \ldots + [\mu_z{}^2-1]M_z{}^2 + M_i S + S'^2)}} \text{ where } S' = S - M_i.
$$

But, on considering the determinant, clearly $(\mu_x{}^2-1)M_x = M_i$. Substituting M_i accordingly

$$
r_{a\eta} = \frac{1}{\mu_a} \frac{S}{\sqrt{(M_i S' + S'^2 + M_i S)}} = \frac{1}{\mu_a}. \tag{18}
$$

[*] This is here assumed to be possible, at any rate if the present theorem is only applied to a finite number of variables. The case of an infinite number has already been demonstrated by (17).

[†] Of course, "element" is here no longer used with the same meaning as previously in this paper.

[‡] Spearman, 'Brit. J. Psych.,' vol. 5, p. 419.

Consequently $r_{ab} - r_{a\eta}r_{b\eta}$ or $r_{\delta_a\delta_b} = 0$.   And extending this result to all the other variables, all of them become actually reduced to the required form of $f_x\eta + \delta_x$, fulfilling all the required conditions.

The practical bearings of some of the foregoing results may be illustrated by reference to the following Table of coefficients, obtained from mental tests applied to 757 children* :—

	Mathematical judgment.	Controlled association.	Literary interpretation.	Selective judgment.	Spelling.
Mathematical judgment ...	—	0·485	0·400	0·397	0·295
Controlled association	0·485	—	0·397	0·397	0·247
Literary interpretation ...	0·400	0·397	—	0·335	0·275
Selective judgment	0·397	0·397	0·335	—	0·195
Spelling	0·297	0·247	0·275	0·195	—

The median value of R_{ab} (even without any correction to compensate for the disturbance by sampling errors) works out at over 0·98.   It thus accords very exactly with the value obtained in (11) and suggests the applicability of the theorem demonstrated in 3 whereby all the correlations will be exclusively due to some single common element.

* The experiments are by Bonser.   They are quoted with reference in 'Brit. Journ. Psych.,' vol. 5, p. 62 (1912).

The Kinetic Theory of a Special Type of Rigid Molecule.

By F. B. Pidduck, M.A., Fellow of Corpus Christi College, Oxford.

1. The present paper is an exercise in the classical kinetic theory, with no admixture of quantum theory, or of the modern theory of atomic structure. The researches of Chapman[*] and Enskog[†] suggest an attempt to see how far exact methods can be used when the molecule has rotational as well as translational energy. It is now well established that if λ is the thermal conductivity, μ the viscosity, and c_v the specific heat at constant volume of a monatomic gas, $\lambda/\mu c_v$ is nearly equal to 2·5. No exhaustive theory is yet in sight for polyatomic gases, but the views of Eucken[‡] are of great interest, and his formula $\lambda/\mu c_v = \frac{1}{4}(9\gamma - 5)$ agrees with many experiments. The present paper discusses the effect of energy of rotation on viscosity and thermal conductivity in a special case, and may help to elucidate certain points, notwithstanding the crudeness of the adopted model.

The need of a molecular model which shall lend itself to calculation has often been felt. In his first paper on the kinetic theory, Maxwell[§] considered the collision of perfectly elastic bodies of any form, and enunciated the theorem about energy of rotation which was afterwards included in the general doctrine of equipartition in the steady state. Of recent years more attention has been paid to slight departures from the steady state, with a view to obtaining a rigorous theory of thermal conductivity, diffusion, and viscosity. Jeans[||] considered the perfectly elastic collisions of smooth spheres whose centres of mass and figure are different. Approximations were made by neglecting powers of r/σ higher than the second, where r is the eccentricity and σ the diameter of the molecule, so that we have rather an unfortunate limiting case in which energy of rotation only adjusts itself infinitely slowly in comparison with that of translation; while the free path phenomena were not treated in detail. It appeared to the writer that there would be less trouble with the molecular model suggested by Bryan.[¶]

* S. Chapman, 'Phil. Trans.,' A, vol. 216, p. 279 (1915) ; vol. 217, p. 115 (1916).

† D. Enskog, 'Inaug. Dissert.,' Upsala, 1917.

‡ A. Eucken, 'Phys. Zeitschr.,' vol. 14, p. 324 (1913).

§ J. C. Maxwell, 'Phil. Mag.' (4), vol. 20, p. 33 (1860) ; 'Collected Papers,' vol. 1, p. 406 ; see also L. Boltzmann, 'Sitzber. Preuss. Akad. Berlin,' p. 1395 (1888) ; 'Wiss. Abhandl.,' vol. 3, p. 366.

|| J. H. Jeans, 'Phil. Trans.,' A, vol. 196, p. 399 (1901) ; 'Quart. J. Math.,' vol. 25, p. 224 (1904).

¶ G. H. Bryan, 'Brit. Ass. Rep.,' p. 83 (1894).

Imagine two spheres to collide and grip each other, so as to bring the points of contact to relative rest. A small elastic deformation is produced, which we suppose to be released immediately afterwards, the force during release being equal to that at the corresponding stage of compression. Thus the relative velocity of the points of contact is reversed by collision.

Let O, O_1 be the centres of two identical molecules of mass M and radius a, P, P_1 the points of impact, $(-MI_x, -MI_y, -MI_z)$ the impulse at P on the first sphere and (MI_x, MI_y, MI_z) the impulse at P_1 on the second sphere. The direction-cosines of OO_1 are taken as (l, m, n). Let

u_x', u_y', u_z' be the linear velocity of the first sphere before collision,

ω_x', ω_y', ω_z' be the angular velocity of the first sphere before collision,

u_{x1}', u_{y1}', u_{z1}' be the linear velocity of the second sphere before collision,

ω_{x1}', ω_{y1}', ω_{z1}' be the angular velocity of the second sphere before collision,

u_x, u_y, u_z be the linear velocity of the first sphere after collision,

ω_x, ω_y, ω_z be the angular velocity of the first sphere after collision,

u_{x1}, u_{y1}, u_{z1} be the linear velocity of the second sphere after collision,

ω_{x1}, ω_{y1}, ω_{z1} be the angular velocity of the second sphere after collision,

and write $\kappa = k^2/a^2$, where k is the radius of gyration of the sphere about any axis through the centroid. Then we have fifteen equations of the five types

$$\left. \begin{array}{ll} u_x' = u_x + I_x, & \omega_x' = \omega_x + \dfrac{mI_z - nI_y}{\kappa a} \\[2mm] u_{x1}' = u_{x1} - I_x, & \omega_{x1}' = \omega_{x1} + \dfrac{mI_z - nI_y}{\kappa a} \end{array} \right\}, \qquad (1)$$

$$u_x' - ma\omega_z' + na\omega_y' - (u_{x1}' + ma\omega_{z1}' - na\omega_{y1}')$$
$$+ u_x - ma\omega_z + na\omega_y - (u_{x1} + ma\omega_{z1} - na\omega_{y1}) = 0. \quad (2)$$

Writing

$$\Theta_x = u_{x1} - u_x + ma(\omega_{z1} + \omega_z) - na(\omega_{y1} + \omega_y), \qquad (3)$$

we find

$$\left. \begin{array}{ll} u_x' = u_x + \dfrac{\kappa \Theta_x l + l(\Theta_x + m\Theta_y + n\Theta_z)}{1 + \kappa}, & \omega_x' = \omega_x + \dfrac{m\Theta_z - n\Theta_y}{a(1 + \kappa)} \\[3mm] u_{x1}' = u_{x1} - \dfrac{\kappa \Theta_x l + l(\Theta_x + m\Theta_y + n\Theta_z)}{1 + \kappa}, & \omega_{x1}' = \omega_{x1} + \dfrac{m\Theta_z - n\Theta_y}{a(1 + \kappa)} \end{array} \right\}. \quad (4)$$

We note the following facts about this collision :—

(1) Accented and unaccented letters can be interchanged in equations (4), with definitions of Θ_x', Θ_y', Θ_z' of the same form as (3); thus equations (3) and (4) can be used also to calculate elements *after* collision from those *before* collision, for a given (l, m, n) physical possibility not being considered. It follows that the (twelfth order) Jacobian of transformation is numerically equal to 1.

(2) The formulæ are unchanged when the signs of l, m, n and the angular velocities are changed, leaving the linear velocities unaltered.

(3) The *rôle* of the two colliding molecules can be interchanged by changing the signs of l, m, n.

(4) There is no gain or loss of kinetic energy by the system.

2. Confining our attention to a single gas, the number of molecules in the volume element $dx\,dy\,dz$ with velocities between u_x, u_y, u_z, and $u_x + du_x$, $u_y + du_y$, $u_z + du_z$, and angular velocities between ω_x, ω_y, ω_z, and $\omega_x + d\omega_x$, $\omega_y + d\omega_y$, $\omega_z + d\omega_z$, is written

$$f\left(t, x, y, z, u_x, u_y, u_z, \omega_x, \omega_y, \omega_z\right) dx\,dy\,dz\,du_x\,du_y\,du_z\,d\omega_x\,d\omega_y\,d\omega_z.$$

The external forces on a molecule are assumed to be statically equivalent to a force (MF_x, MF_y, MF_z), at the centre, where F is independent of the velocity.[*] Direct collision between molecules $(u_x, u_y, u_z, \omega_x, \omega_y, \omega_z)$ and $(u_{x1}, u_{y1}, u_{z1}, \omega_{x1}, \omega_{y1}, \omega_{z1})$ is not possible with the direction-cosines l, m, n of equation (4), the direction-cosines $-l$, $-m$, $-n$ taking their place. The proof of the equation satisfied by f is well known.[†] The later proofs are free from a defect pointed out by Lorentz,[‡] which would be quite fatal with a rigid molecule. Thus the direct collision just referred to does not give linear and angular velocities $(u_x', u_y', u_z', \omega_x', \omega_y', \omega_z')$ and $(u_{x1}', u_{y1}', u_{z1}', \omega_{x1}', \omega_{y1}', \omega_{z1}')$ after collision; the nearest thing to an inverse collision is that molecules $(u_x, u_y, u_z, -\omega_x, -\omega_y, -\omega_z)$ and $(u_{x1}, u_{y1}, u_{z1}, -\omega_{x1}, -\omega_{y1}, -\omega_{z1})$, colliding at $(-l, -m, -n)$, give molecules $(u_x', u_y', u_z', -\omega_x', -\omega_y', -\omega_z')$ and $(u_{x1}', u_{y1}', u_{z1}', -\omega_{x1}' -\omega_{y1}' -\omega_{z1}')$ (see notes (1) and (2) of last article).

Writing $d\tau$ for the expression $du_x du_y du_z d\omega_x d\omega_y d\omega_z$ and $d\tau_1$ for $du_{x1} du_{y1} du_{z1} d\omega_{x1} d\omega_{y1} d\omega_{z1}$ we have

$$\int \left(f'f_1' - ff_1\right) V\sigma^2\,dS\,d\tau_1 = \frac{\partial f}{\partial t} + u_x\frac{\partial f}{\partial x} + u_y\frac{\partial f}{\partial y} + u_x\frac{\partial f}{\partial z}$$

$$+ F_x\frac{\partial f}{\partial u_x} + F_y\frac{\partial f}{\partial u_y} + F_z\frac{\partial f}{\partial u_z}, \quad (5)$$

where

$$V = l\left(u_{x1} - u_x\right) + m\left(u_{y1} - u_y\right) + n\left(u_{z1} - u_z\right). \quad (6)$$

Here $\sigma = 2a$ is the diameter of the molecule and dS an element of solid angle in the direction (l, m, n), integration with respect to S being over that hemisphere which makes V positive.

* For the general case see H. A. Lorentz, 'Abhandlungen über theoretische Physik,' vol. 1, p. 164 (1907).

† L. Boltzmann, 'Wien. Ber.,' vol. 66, Abth. 2, p. 324 (1872) ; vol. 72, p. 427 (1875); 'Wiss. Abhandl.,' vol. 1, p. 361 ; vol. 2, p. 1 ; 'Gastheorie,' vol. 1, p. 98.

‡ H. A. Lorentz, 'Wien. Ber.,' vol. 95, Abth. 2, p. 115 (1887); L. Boltzmann, *ibid.*, p. 153.

The advantages of Bryan's model will now be apparent. We have no angular positional co-ordinates in the equation, and no $\partial/\partial\omega$ terms on the right. From $\int (f'f_1' - ff_1)\,V dS d\tau_1 = 0$ in the equilibrium state we pass to $f'f_1' = ff_1$ for all possible collisions, notes (1) and (3) of Article 1 justifying the transformation of the integral

$\int \phi\,(f'f_1' - ff_1)\,V dS d\tau d\tau_1$ to $-\tfrac{1}{4}\int (\phi' + \phi_1' - \phi - \phi_1)\,(f'f_1' - ff_1)\,V dS d\tau d\tau_1.$*

Hence the distribution

$$\log f = \lambda \{u_x^2 + u_y^2 + u_z^2 + \kappa a^2 (\omega_x^2 + \omega_y^2 + \omega_z^2)\} + \mu u_x + \nu u_y + \rho u_z + \sigma \quad (7)$$

is sufficient for equilibrium, though not proved to be necessary.

In a paper on the kinetic theory of a gas whose molecules are smooth rigid bodies of any form, Ishida† finds also linear terms in ω, but his reasoning seems to depend on an erroneous inclusion of the angular momentum of a molecule round its centroid in the class of summational invariants. The linear terms are said to be determined by the visible motion of rotation of the gas. With our present model, at least, there are weighty reasons against this; firstly, that excess angular velocity of one sign tends (unlike excess linear velocity) to disappear when two molecules collide; and, secondly, that for a gas rotating uniformly in a cylindrical vessel there is no need to assume a unilateral distribution of angular velocity. To prove the first point consider two groups of molecules with definite linear and angular velocities, which are within narrow limits of $(u_x, u_y, u_z, \omega_x, \omega_y, \omega_z)$ and $(u_{x1}, u_{y1}, u_{z1}, \omega_{x1}, \omega_{y1}, \omega_{z1})$ respectively. The number of collisions in which the line of centres is within an elementary solid angle dS near (l, m, n) is proportional to $V dS$, and we have to find the mean angular velocity after collision. Write

$$\alpha_x = \omega_{x1} + \omega_x, \ldots\ldots \Phi_x = u_{x1} - u_x, \ldots\ldots.$$

Then (3) and (4) give three equations of the type

$$\alpha_x' = \left\{1 - \frac{2}{1+\kappa}\,(m^2 + n^2)\right\} \alpha_x + \frac{2}{1+\kappa}\,(lm\alpha_y + nl\alpha_z)$$
$$+ \frac{2}{a(1+\kappa)}\,(m\Phi_z - n\Phi_y).$$

Take axes for the moment so that $\Phi_x = \Phi_y = 0$ and Φ_z is positive. Then

$$\alpha_x' = \left\{1 - \frac{2}{1+\kappa}\,(m^2 + n^2)\right\} \alpha_x + \frac{2}{1+\kappa}\,(lm\alpha_y + nl\alpha_z) + \frac{2m\Phi_z}{a(1+\kappa)},$$

$$\alpha_y' = \left\{1 - \frac{2}{1+\kappa}\,(n^2 + l^2)\right\} \alpha_y + \frac{2}{1+\kappa}\,(mn\alpha_z + lm\alpha_x) - \frac{2l\Phi_z}{a(1+\kappa)},$$

$$\alpha_z' = \left\{1 - \frac{2}{1+\kappa}\,(l^2 + m^2)\right\} \alpha_z + \frac{2}{1+\kappa}\,(nl\alpha_x + mn\alpha_y).$$

* *Cf.* Boltzmann, 'Gastheorie,' vol. 1, pp. 119–121; Enskog, p. 24.
† Y. Ishida, 'Phys. Rev.,' vol. 10, p. 317 (1917).

We have $V = \Phi n_z$ *and integration is over the hemisphere* $n > 0$. *The mean values of* α_x', α_y', α_z' *are given by*

$$\pi \alpha_x' = \int \alpha_x' n dS, \qquad \pi \alpha_y' = \int \alpha_y' n dS, \qquad \pi \alpha_z' = \int \alpha_z' n dS.$$

Terms after the first in the expressions for α_x', α_y', α_z' vanish on integration, so that

$$\pi \alpha_x' = \alpha_x \int \left\{ n - \frac{2n}{1+\kappa} (m^2 + n^2) \right\} dS, \quad \pi \alpha_y' = \alpha_y \int \left\{ n - \frac{2n}{1+\kappa} (n^2 + l^2) \right\} dS,$$

$$\pi \alpha_z' = \alpha_z \int \left\{ n - \frac{2n}{1+\kappa} (l^2 + m^2) \right\} dS.$$

Evaluating the integrals,

$$\alpha_x' = \left\{ 1 - \frac{3}{2(1+\kappa)} \right\} \alpha_x, \qquad \alpha_y' = \left\{ 1 - \frac{3}{2(1+\kappa)} \right\} \alpha_y,$$

$$\alpha_z' = \left\{ 1 - \frac{1}{1+\kappa} \right\} \alpha_z.$$

Each of the three coefficients being numerically less than unity, the magnitude of the mean angular velocity after collision is less than $(\alpha_x^2 + \alpha_y^2 + \alpha_z^2)^{\frac{1}{2}}$.

As regards mass-rotation of the gas as a whole, the case of a monatomic gas rotating with uniform angular velocity is one of those for which Boltzmann[*] found an exact solution, and the proof applies also to the present molecular model. Boltzmann's solutions make both the left and right-hand sides of his equation (5) vanish. As far as the left-hand side is concerned, λ, μ, ν, ρ and σ in equation (7) may be any functions of x, y, z and t. The right-hand side vanishes if

$$\lambda, \sigma = \text{const.}, \quad \mu = y\Omega_z - z\Omega_y, \quad \nu = z\Omega_x - x\Omega_z, \quad \rho = x\Omega_y - y\Omega_x,$$

where Ω_x, Ω_y, Ω_z are constants, and the mass-motion is a uniform rotation with angular velocity $-\Omega/2\lambda$. Thus rotation of the gas as a whole does not necessarily imply preponderant rotation of the separate molecules about any axis.

3. The general idea underlying all recent theories of viscosity and thermal conduction in gases is that of successive approximation, initiated by Maxwell[†] and applied to Boltzmann's equation by Brillouin,[‡] Lorentz,[§] and

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[*] L. Boltzmann, 'Wien. Ber.,' vol. 74, Abth. 2, p. 539 (1876); 'Wiss. Abhandl.,' vol. 2, p. 90; 'Gastheorie,' vol. 1, p. 130.

[†] J. C. Maxwell, 'Phil. Trans.,' vol. 157, p. 80 (1866); 'Collected Papers,' vol. 2, p. 68.

[‡] M. Brillouin, 'Ann. Chim. Phys.,' (7), vol. 20, p. 451 (1900).

[§] H. A. Lorentz, 'Archives Néerland.,' vol. 10, p. 343 (1905); 'Theory of Electrons,' 2nd ed., p. 267.

Hilbert[*] Hilbert's argument is essentially as follows. Writing D for the operator

$$\frac{\partial}{\partial t}+u_x\frac{\partial}{\partial x}+u_y\frac{\partial}{\partial y}+u_z\frac{\partial}{\partial z}+F_x\frac{\partial}{\partial u_x}+F_y\frac{\partial}{\partial u_y}+F_z\frac{\partial}{\partial u_z}, \qquad (8)$$

equation (5) becomes

$$\int (f'f_1'-ff_1)\,V dS\,d\tau_1 = \frac{1}{\sigma^2}\,Df.$$

Expanding f in the form

$$f = \Phi+\frac{\Psi}{\sigma^2}+\frac{X}{\sigma^4}+\dots,$$

and equating coefficients of the various powers of $1/\sigma^2$, we have a set of equations to determine Φ, Ψ, ..., of which the first two are

$$\int (\Phi'\Phi_1'-\Phi\Phi_1)\,V\,dS\,d\tau_1 = 0, \qquad (9)$$

$$\int (\Phi_1'\Psi'+\Phi'\Psi_1'-\Phi_1\Psi-\Phi\Psi_1)\,V\,dS\,d\tau_1 = D\Phi. \qquad (10)$$

For the solution of (9) we take

$$\Phi = \frac{\rho M^2 a^3 \kappa^{3/2}}{8\pi^3 R^3 T^3}$$
$$\exp\left[-\frac{M}{2RT}\left\{(u_x-v_x)^2+(u_y-v_y)^2+(u_z-v_z)^2+\kappa a^2(\omega_x^2+\omega_y^2+\omega_z^2)\right\}\right],$$
$$(11)$$

where ρ is the density, T the absolute temperature and (v_x, v_y, v_z) the mean velocity of the gas at (x, y, z) at time t, and R the universal gas constant $1\cdot35\times10^{-16}$. This choice of parameters makes $\int f\psi\,d\tau = \int \Phi\psi\,d\tau$ for any of the five functions

$$\psi = 1, \quad u_x, \quad u_y, \quad u_z, \quad u_x^2+u_y^2+u_z^2+\kappa a^2(\omega_x^2+\omega_y^2+\omega_z^2).$$

Following Brillouin and Hilbert we write $\Psi = \Phi\phi$, so that we have to the first order in $1/\sigma^2$

$$f = \Phi(1+\phi/\sigma^2), \qquad (12)$$

where ϕ is given by the equation

$$\int \Phi_1(\phi'+\phi_1'-\phi-\phi_1)\,V\,dS\,d\tau_1 = D(\log \Phi), \qquad (13)$$

and satisfies the additional conditions

$$\int \Phi\phi\,d\tau = \int \Phi\phi u_x\,d\tau = \int \Phi\phi u_y\,d\tau = \int \Phi\phi u_z\,d\tau$$
$$= \int \Phi\phi\{u_x^2+u_y^2+u_z^2+\kappa a^2(\omega_x^2+\omega_y^2+\omega_z^2)\}\,d\tau = 0. \quad (14)$$

* D. Hilbert, 'Math. Ann.,' vol. 72, p. 565 (1912); 'Lineare Integralgleichungen,' p. 270.

4. Following Hilbert and Enskog, it is convenient to introduce the new variables

$$p_x = \left(\frac{M}{2RT}\right)^{\frac{1}{2}} (u_x - v_x), \quad p_y = \left(\frac{M}{2RT}\right)^{\frac{1}{2}} (u_y - v_y), \quad p_z = \left(\frac{M}{2RT}\right)^{\frac{1}{2}} (u_z - v_z)$$

$$q_x = \left(\frac{M\kappa}{2RT}\right)^{\frac{1}{2}} a\omega_x, \qquad q_y = \left(\frac{M\kappa}{2RT}\right)^{\frac{1}{2}} a\omega_y, \qquad q_z = \left(\frac{M\kappa}{2RT}\right)^{\frac{1}{2}} a\omega_z$$

$$\Big\}, \quad (15)$$

and write

$$p^2 = p_x^2 + p_y^2 + p_z^2, \quad q^2 = q_x^2 + q_y^2 + q_z^2, \quad dr = dp_x\, dp_y\, dp_z\, dq_x\, dq_y\, dq_z, \quad (16)$$

$$\frac{d}{dt} \equiv \frac{\partial}{\partial t} + v_x \frac{\partial}{\partial x} + v_y \frac{\partial}{\partial y} + v_z \frac{\partial}{\partial z}. \quad (17)$$

Then if no external forces are acting, equation (13) becomes

$$\int \exp\left(-p_1^2 - q_1^2\right)(\phi' + \phi_1' - \phi - \phi_1)\, V\, dS\, dr_1$$

$$= \frac{M\pi^3}{\rho} \left[\left(\frac{M}{2RT}\right)^{\frac{1}{2}} \frac{d}{dt} \log\left(\frac{\rho}{T^3}\right) + \left(\frac{M}{2RT}\right)^{\frac{1}{2}} \frac{p^2 + q^2}{T} \frac{dT}{dt} \right.$$

$$+ \frac{M}{RT} \left(p_x \frac{dv_x}{dt} + p_y \frac{dv_y}{dt} + p_z \frac{dv_z}{dt}\right)$$

$$+ \left(p_x \frac{\partial}{\partial x} + p_y \frac{\partial}{\partial y} + p_z \frac{\partial}{\partial z}\right) \log\left(\frac{\rho}{T^3}\right) + \frac{p^2 + q^2}{T} \left(p_x \frac{\partial T}{\partial x} + p_y \frac{\partial T}{\partial y} + p_z \frac{\partial T}{\partial z}\right)$$

$$\left. + 2\left(\frac{M}{2RT}\right)^{\frac{1}{2}} \left\{ p_x^2 \frac{\partial v_x}{\partial x} + \ldots + \ldots + p_y p_z \left(\frac{\partial v_z}{\partial y} + \frac{\partial v_y}{\partial z}\right) + \ldots + \ldots \right\} \right], \quad (18)$$

where we write with a slight change of notation

$$V = l\,(p_{x1} - p_x) + m\,(p_{y1} - p_y) + n\,(p_{z1} - p_z). \quad (19)$$

With a similar slight change in equations (3) and (4) we have

$$p_x' = p_x + \frac{\kappa\Theta_x + lV}{1 + \kappa}, \qquad q_x' = q_x + \frac{\kappa^{\frac{1}{2}}(m\Theta_z - n\Theta_y)}{1 + \kappa}$$

$$p_{x1}' = p_{x1} - \frac{\kappa\Theta_x + lV}{1 + \kappa}, \qquad q_{x1}' = q_{x1} + \frac{\kappa^{\frac{1}{2}}(m\Theta_z - n\Theta_y)}{1 + \kappa}$$

$$\Big\} \quad (20)$$

where $\qquad \Theta_x = p_{x1} - p_x + \kappa^{-\frac{1}{2}} m\,(q_{z1} + q_z) - \kappa^{-\frac{1}{2}} n\,(q_{y1} + q_y). \quad (21)$

In order that equations (18) may be soluble, certain conditions must be satisfied, which, as Hilbert pointed out, are the approximate hydrodynamical equations, together with the equations of continuity and energy. Writing Q for the right-hand side of equation (18), we have

$$\int \exp\left(-p^2 - q^2\right) Q\psi\, dr$$

$$= \int \exp\left(-p^2 - q^2 - p_1^2 - q_1^2\right)(\phi' + \phi_1' - \phi - \phi_1)\, \psi V dS\, dr\, dr_1,$$

where ψ is an arbitrary function of $p_x, p_y, p_z, q_x, q_y, q_z$, subject to certain

conditions of integrability. Writing $[\phi, \psi]$, in Enskog's notation, for the integral on the right, we find as before

$$[\phi, \psi] = -\tfrac{1}{4} \int \exp(-p^2 - q^2 - p_1^2 - q_1^2)$$
$$(\phi' + \phi_1' - \phi - \phi_1)(\psi' + \psi_1' - \psi - \psi_1) \, V \, dS \, dr \, dr_1,$$

showing that $[\phi, \psi] = [\psi, \phi]$. It follows that necessary conditions for the solubility of (18) are $\int \exp(-p^2 - q^2) Q \psi \, dr = 0$, where ψ is any of the functions $1, p_x, p_y, p_z, p^2 + q^2$. The right-hand side of (18) is of the form

$$Q = Q_{00} + Q_0(p^2 + q^2) + \{Q_{x0} + Q_x(p^2 + q^2)\}p_x + \cdots$$
$$+ Q_{xx}p_x^2 + \cdots + Q_{yz}p_y p_z + \cdots,$$

where the coefficients $Q_{00}, \ldots$ are independent of $p_x, p_y, p_z, q_x, q_y, q_z$. Evaluating the integrals we find

$$Q_{00} = 0, \qquad Q_0 = -\tfrac{1}{6}(Q_{xx} + Q_{yy} + Q_{zz}), \qquad Q_{x0} = -4Q_x,$$
$$Q_{y0} = -4Q_y, \qquad Q_{z0} = -4Q_z.$$

Using these equations to remove the d/dt terms from (18), it becomes

$$\int \exp(-p_1^2 - q_1^2)(\phi' + \phi_1' - \phi - \phi_1) \, V \, dS \, dr_1$$
$$= Q_x(p^2 + q^2 - 4)p_x + \cdots + Q_{xx}\{p_x^2 - \tfrac{1}{6}(p^2 + q^2)\}$$
$$+ \cdots + Q_{yz}p_y p_z + \cdots, \quad (22)$$

where

$$Q_x = \frac{M\pi^3}{\rho}\frac{1}{T}\frac{\partial T}{\partial x}, \qquad Q_{xx} = \frac{2M\pi^3}{\rho}\left(\frac{M}{2RT}\right)^{\frac{1}{2}}\frac{\partial v_x}{\partial x},$$
$$Q_{yz} = \frac{2M\pi^3}{\rho}\left(\frac{M}{2RT}\right)^{\frac{1}{2}}\left(\frac{\partial v_z}{\partial y} + \frac{\partial v_y}{\partial z}\right). \quad (23)$$

It remains to limit the form of ϕ.[*] We must have by consideration of orthogonal invariance, with due regard to (14),

$$\phi = Q_x\phi_x + Q_y\phi_y + Q_z\phi_z + Q_{xx}\phi_{xx} + \cdots + Q_{yz}\phi_{yz} + \cdots, \quad (24)$$

where

$$\left. \begin{array}{l} \phi_x = P_0 p_x + P_1 q_x \\ \phi_{xx} = P_2(p_x^2 - \tfrac{1}{3}p^2) + P_3\{p_x q_x - \tfrac{1}{3}(p_x q_x + p_y q_y + p_z q_z)\} + P_4(q_x^2 - \tfrac{1}{3}q^2) \\ \phi_{yz} = P_2 p_y p_z + P_3(p_y q_z + p_z q_y) + P_4 q_y q_z \end{array} \right\}, \quad (25)$$

and $P_0, \ldots P_4$ are functions of $p^2, q^2, p_x q_x + p_y q_y + p_z q_z$ only. Writing

$$I(\phi) \equiv \int \exp(-p_1^2 - q_1^2)(\phi' + \phi_1' - \phi - \phi_1) \, V \, dS \, dr_1, \quad (26)$$

the functions $P_0, \ldots$ have to be found from the equations

$$\left. \begin{array}{l} I(\phi_x) = (p^2 + q^2 - 4)p_x \\ I(\phi_{xx}) = p_x^2 - \tfrac{1}{6}(p^2 + q^2) \end{array} \right\}. \quad (27)$$

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[*] *Cf.* Brillouin, *loc. cit.*; H. A. Lorentz, 'Vorträge über die kinetische Theorie der Materie,' p. 185 (1914).

Equations (14) may be written

$$\int \exp\left(-p^2 - q^2\right) \phi \psi \, dr = 0 \left.\right\}$$

where
$$\psi = 1, \ p_x, \ p_y, \ p_z, \ p^2 + q^2 \left.\right\}.$$
(28)

5. Following Enskog, we attempt a series solution of (27). The functions are made to satisfy (28), and are of the following types :—

Conductivity type.

(1) $\phi = \left[p^{2r} q^{2s} (p_x q_x + p_y q_y + p_x q_z)^{2t} - \dfrac{8\,\Gamma\left(r + t + \frac{5}{2}\right)\Gamma\left(s + t + \frac{3}{2}\right)}{3\pi\,(2t+1)} \right] p_x,$

(2) $\phi = p^{2r} q^{2s} (p_x q_x + p_y q_y + p_z q_z)^{2t+1} p_x,$

(3) $\phi = p^{2r} q^{2s} (p_x q_x + p_y q_y + p_z q_z)^{2t} q_x,$

(4) $\phi = \left[p^{2r} q^{2s} (p_x q_x + p_y q_y + p_x q_z)^{2t+1} \right.$

$\left. \qquad - \dfrac{16\,\Gamma\left(r + t + \frac{3}{2}\right)\Gamma\left(s + t + \frac{5}{2}\right)}{3\pi\,(2t+3)} (p_x q_x + p_y q_y + p_x q_z) \right] q_x.$

Viscosity type.

(1) $\phi = p^{2r} q^{2s} (p_x q_x + p_y q_y + p_x q_z)^{t} \left(p_x^2 - \frac{1}{3} p^2\right),$

(2) $\phi = p^{2r} q^{2s} (p_x q_x + p_y q_y + p_x q_z)^{t} \left(q_x^2 - \frac{1}{3} q^2\right),$

(3) $\phi = p^{2r} q^{2s} (p_x q_x + p_y q_y + p_x q_z)^{t} \left\{ p_x q_x - \frac{1}{3} (p_x q_x + p_y q_y + p_x q_z) \right\}.$

To solve the first of equations (27) write

$$\phi_x = \Sigma c_n \phi_n,$$
(29)

where c_1, c_2, ... are constant coefficients and ϕ_1, ϕ_2, ... functions of the conductivity type. Write also

$$\alpha_n = \int \exp\left(-p^2 - q^2\right)(p^2 + q^2 - 4)\,p_x \phi_n \, dr \left.\right\}$$
$$a_{mn} = a_{nm} = [\phi_m, \phi_n] = \int \exp\left(-p^2 - q^2\right) \mathrm{I}\,(\phi_m)\,\phi_n \, dr \left.\right\}.$$
(30)

Then the quantities α_n, a_{mn} are known by quadrature, and (27) gives

$$c_1 a_{11} + c_2 a_{12} + \ldots = \alpha_1 \left.\right\}$$
$$c_1 a_{21} + c_2 a_{22} + \ldots = \alpha_2 \left.\right\}.$$
$$\ldots\ldots\ldots\ldots$$
(31)

These are the equations for the assumed coefficients. Chapman and Enskog have shown that terms of the first three degrees account for about 98 per cent. of the thermal conductivity and viscosity of a monatomic gas. It will be convenient, though not theoretically necessary, to neglect terms of degree higher than the third, thus obtaining a theory of the same approximation as Chapman's first theory.* We take

$$\phi_1 = (p^2 - \tfrac{5}{2})p_x, \quad \phi_2 = (q^2 - \tfrac{3}{2})p_x, \quad \phi_3 = (p_x q_x + p_y q_y + p_x q_z) p_x \left.\right\}$$
$$\phi_4 = q_x, \qquad\qquad \phi_5 = p^2 q_x, \qquad\qquad \phi_6 = q^2 q_x \left.\right\}.$$
(32)

* S. Chapman, ' Phil. Trans.,' A, vol. 211, p. 433 (1911).

Evaluation of the integrals (30) is simplified by observing that only even powers of $\kappa^{\frac{1}{2}}$ occur in $I(\phi_n)$, since the change from $\kappa^{\frac{1}{2}}$ to $\kappa^{-\frac{1}{2}}$ merely interchanges the *rôle* of two colliding molecules. The work is not laborious, but would become so if carried to a higher degree than the third. We find

$$\alpha_1 = \tfrac{5}{4}\pi^3, \qquad \alpha_2 = \tfrac{3}{4}\pi^3, \qquad \alpha_3 = \alpha_4 = \alpha_5 = \alpha_6 = 0,$$

$$a_{11} = -\frac{(17\kappa+4)(2\pi)^{\frac{1}{2}}\pi^6}{3(1+\kappa)^2}, \quad a_{12} = \frac{5\kappa(2\pi)^{\frac{1}{2}}\pi^6}{3(1+\kappa)^2}, \quad a_{13} = a_{14} = a_{15} = a_{16} = 0,$$

$$a_{21} = \frac{5\kappa(2\pi)^{\frac{1}{2}}\pi^6}{3(1+\kappa)^2}, \qquad a_{22} = -\frac{(2\kappa^2+2\kappa+1)(2\pi)^{\frac{1}{2}}\pi^6}{(1+\kappa)^2},$$

$$a_{23} = a_{24} = a_{25} = a_{26} = 0,$$

$$\tag{33}$$

It follows that $c_3 = c_4 = c_5 = c_6 = 0$, and c_1, c_2 are given by the equations

$$c_1 a_{11} + c_2 a_{12} = \alpha_1, \qquad c_1 a_{21} + c_2 a_{22} = \alpha_2.$$

Hence

$$c_1 = -\frac{30\kappa^2+45\kappa+15}{102\kappa^3+101\kappa^2+75\kappa+12} \frac{3(1+\kappa)^2}{4\pi^3(2\pi)^{\frac{1}{2}}},$$

$$c_2 = -\frac{76\kappa+12}{102\kappa^3+101\kappa^2+75\kappa+12} \frac{3(1+\kappa)^2}{4\pi^3(2\pi)^{\frac{1}{2}}}. \tag{34}$$

To deal with viscosity we write $\phi_{xx} = c_7\phi_7 + c_8\phi_8 + c_9\phi_9$, where

$$\phi_7 = p_x^2 - \tfrac{1}{3}p^2, \quad \phi_8 = q_x^2 - \tfrac{1}{3}q^2, \quad \phi_9 = p_x q_x - \tfrac{1}{3}(p_x q_x + p_y q_y + p_z q_z) \tag{35}$$

and

$$\alpha_n = \int \exp(-p^2-q^2)\{p_x^2 - \tfrac{1}{6}(p^2+q^2)\}\phi_n\, dr, \tag{36}$$

a_{mn} remaining as in (30). We find

$$\alpha_7 = \tfrac{1}{3}\pi^3, \qquad \alpha_8 = \alpha_9 = 0,$$

$$a_{77} = -\frac{4(13\kappa+6)(2\pi)^{\frac{1}{2}}\pi^6}{45(1+\kappa)^2}, \qquad a_{78} = a_{79} = 0 \left.\right\} \cdot \tag{37}$$

Thus to our present order of approximation $\phi_{xx} = c_7\phi_7$, where

$$c_7 = -\frac{15(1+\kappa)^2}{4(13\kappa+6)\pi^3(2\pi)^{\frac{1}{2}}}. \tag{38}$$

6. Considering only the Q_x term in (24), the heat flow per cm.² (in mechanical units) is

$$\tfrac{1}{2}M \int f(u_x - v_x)\{(u_x - v_x)^2 + (u_y - v_y)^2 + (v_x - v_z)^2 + \kappa a^2(\omega_x^2 + \omega_y^2 + \omega_z^2)\}\, d\tau,$$

where

$$f = \Phi + \frac{M^3 a^3 \kappa^{3/2}}{8R^3 T^4 \sigma^2}\frac{\partial T}{\partial x}\exp(-p^2-q^2)(c_1\phi_1 + c_2\phi_2),$$

from (12) and (29). The first term in f contributes nothing to the flow.

Replacing $\partial T/\partial x$ by -1, we have an expression for the thermal conductivity, which becomes on reduction

$$\lambda = -\frac{\pi^3}{4\sigma^2}\left(\frac{2R^3T}{M}\right)^{\frac{1}{2}}(5c_1+3c_2),$$

or

$$\lambda = \frac{9}{16\sigma^2}\left(\frac{R^3T}{\pi M}\right)^{\frac{1}{2}}\frac{(1+\kappa)^2(50\kappa^2+151\kappa+37)}{102\kappa^3+101\kappa^2+75\kappa+12}. \tag{39}$$

The case in which $\kappa \to \infty$ is of no physical importance, but it is curious to see why $\lambda \to \infty$ in this case. Rotational motion is practically absent, and the effect of a collision from (4) is to transfer each velocity to the other molecule, virtually as if there had been no collision at all. The conductivity has a finite limit as $\kappa \to 0$, notwithstanding that $\omega \to \infty$ in the steady state.

Considering only the viscosity terms in (24), the X_x component of stress in the gas is given by

$$X_x - p = M\int f\left[(u_x-v_x)^2 - \tfrac{1}{3}\left\{(u_x-v_x)^2+(u_y-v_y)^2+(u_z-v_z)^2\right\}\right]d\tau$$

$$= \frac{M\pi^3}{3\sigma^2}\left(\frac{2RT}{M}\right)^{\frac{1}{2}}c_7\left(2\frac{\partial v_x}{\partial x}-\frac{\partial v_y}{\partial y}-\frac{\partial v_z}{\partial z}\right)$$

on reduction. Identifying the coefficient of $2\dfrac{\partial v_x}{\partial x}-\dfrac{\partial v_y}{\partial y}-\dfrac{\partial v_z}{\partial z}$ with $-\tfrac{2}{3}\mu$ and substituting from (38) we have

$$\mu = \frac{15}{8\sigma^2}\left(\frac{MRT}{\pi}\right)^{\frac{1}{2}}\frac{(1+\kappa)^2}{13\kappa+6}. \tag{40}$$

Also $c_v = 3R/M$, so that

$$\frac{\lambda}{\mu c_v} = \frac{(13\kappa+6)(50\kappa^2+151\kappa+37)}{10(102\kappa^3+101\kappa^2+75\kappa+12)}. \tag{41}$$

For $\kappa = 0, \tfrac{2}{3}$, and 1 we have $\lambda/\mu c_v = 1\cdot85, 1\cdot82, 1\cdot56$ respectively. Eucken's value corresponding to $\gamma = \tfrac{4}{3}$ is $\lambda/\mu c_v = 1\cdot75$; experiment gives $\gamma = 1\cdot33$ and $\lambda/\mu c_v = 1\cdot80$ for chlorine. It is not intended to suggest that the evidence supports any particular model; only that Eucken's number is as well confirmed as we can expect, seeing that $\lambda/\mu c_v$ does not depend on γ alone. Qualitative writers have often conjectured that viscosity is but little affected by rotation of the molecule. With our model, μ changes in the ratio $1:1\cdot26$ as κ changes from 0 to 1, and the lower value is the same as that of a monatomic gas in Chapman's first approximation. Another much debated matter is the partition of transported energy between the translational and rotational kinds in thermal conduction. As far as our theory goes, we find

$$\frac{\text{transported rotational energy}}{\text{transported translational energy}} = \frac{4(19\kappa+3)}{25(2\kappa^2+3\kappa+1)}, \tag{42}$$

which changes from 0·48 to 0·59 as κ changes from 0 to 1, with a maximum of 0·67 in between. It is difficult to imagine a model more effective in converting linear into angular velocity, and *vice versâ*, so that 70 per cent. may well be an upper limit of the relative efficiency of transport of rotational and translational energy.

The Specific Heats of Air, Steam and Carbon Dioxide.

By Sir R. T. GLAZEBROOK, F.R.S.

In a recent number[*] is a paper by Mr. W. D. Womersley bearing the above title, in which an account is given of a determination of specific heats of the gases named, employing a calorimeter designed by the late Prof. B. Hopkinson.

Mr. Womersley's experiments extended over the range 1000° C. to 2000°, and he states that the lower parts have been filled in from the researches of Swann and Holborn and Henning.

The results are given in a Table on p. 486 for every 100° C. up to 2000°. Swann's experiments were made at temperatures of 20° C. and 100° C., so that the range of values from 200° to 1000° depends on the work of Holborn and Henning, and, unfortunately, some error has been made in connection with their results.

They expressed these as the mean specific heat at constant pressure between 0° C. and the temperature of the observation—in the case of steam between 100° C. and the observation temperature.

Mr. Womersley has transformed their figures into mean volumetric heat per gramme-molecule, but I have been unable to deduce his figures from those given by Holborn and Henning, and, in view of the importance of the matter, it seems desirable to call attention to the discrepancy.

Holborn and Henning, in their paper,[†] give—Table VIII—their experimental results, and also the results obtained from a formula which expresses the experimental results within, in most cases less than 1 per cent. In the case of steam, two formulæ, which differ but slightly, are given, while in Table IX (p. 842) are stated the results at every 200° C. up to 1400° C.

[*] 'Roy. Soc. Proc.,' A, vol. 100, p. 483.
[†] 'Annalen des Physik,' vol. 23, p. 809 (1907).

. *I have reduced these last to volumetric heats per gramme-molecule in each case by multiplying by 28, 18 and 44 respectively and subtracting 1·985, the difference between the volumetric heats at constant pressure and constant volume.*

The results are given in the second, fourth and sixth columns of Table I. In the third, fifth and seventh columns are values taken from Mr. Womersley's Table, which in the range 200° to 1000° are said to " be filled in from the researches of . . . Holborn and Henning." The differences are very considerable, amounting to from 6 to 8 per cent.

The figures at the higher temperatures given in these columns are the results of Mr. Womersley's own experiments. It will be noticed that these are higher than the corresponding figures due to Holborn.

Table I.

Tem-perature.	Nitrogen.		Steam.		Carbon dioxide.	
	Holborn.	Womersley.	Holborn.	Womersley.	Holborn.	Womersley.
° C.						
200	4·70	5·00	6·30	6·61	7·48	7·5
400	4·81	5·177	6·43	6·70	8·04	8·35
600	4·91	5·332	6·52	6·85	8·51	9·03
800	5·02	5·471	6·69	7·02	8·98	9·56
1000	5·13	5·590	6·91	7·29	9·33	9·94
1200	5·23	5·698	7·20	7·75	9·64	10·21
1400	5·34	5·766	7·55	8·35	9·88	10·41

In an appendix to the Report of the B.A. Committee on Gaseous Explosives for 1908, the opinion is expressed that the values given by Holborn and Henning are too low, and this may be the case, but that fact will not explain why the high values given in Mr. Womersley's Table for the range 200° C. to 1000° C. are assigned to these authors.

With regard to Mr. Womersley's own values, it is no doubt difficult to discuss their accuracy from the small-scale diagrams (figs. 4 and ·5), in which the slopes of the various lines give the volumetric heats—Mr. Womersley doubtless used large diagrams—but the points are in many cases scattered somewhat too widely to justify the accuracy of 1 to 2 per cent. which is claimed, and in some cases—*e.g.,* fig. 4, the curves for 1800° and 1600°—lines could be drawn of distinctly less slope, which would represent the experimental results more closely.

The values deduced above from Holborn and Henning's results agree

closely with those given by Piers and Bjerram* in various papers in the 'Zeitschrift für Electrochemie' in 1911 and 1912, of which a summary was given by Pye in the 'Automobile Engineer' for February, 1920.

Mr. Womersley states that, at the time the experiments were initiated and carried out, Bjerram's corrections to Pier's results had not arrived; they were to hand before the date of the paper, August, 1921.

A Photographic Spectrum of the Aurora of May 13-15, 1921, and Laboratory Studies in Connection with it.

By LORD RAYLEIGH, F.R.S.

[PLATE 2.]

§ 1. Aurora of May 13-15.

On May 13, 1921, and the following days, there was a magnetic storm of almost unprecedented violence, connected without doubt with a large and highly eruptive spot near the centre of the sun's disc.

At the time I was systematically photographing the spectrum of the diffused light of the sky every night for the investigation of the faint aurora line ordinarily present.[†] The instrument used was the spectrograph No. 1[‡] having a Rutherford prism, and a cinematograph lens of 3 inches focus, working at $F/1.9$. An orthochromatic plate was used. The direction of view was 45° up to the north.

On developing the photograph of May 13 (*i.e.*, begun on the evening of that day) it was found that the nitrogen negative bands had come up strongly, as well as the green aurora line. This was the first intimation I had that anything unusual was in progress, and the day of May 14 was spent in preparing as far as possible for an extended programme if the aurora should continue. Two additional spectrographs were extemporised. The aurora *did* continue on the night of May 14, and presumably throughout the intervening day. Another and somewhat stronger photograph on an orthochromatic plate was got with the Rutherford prism instrument used before.

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* Such small differences as there are appear to be due to the fact that Bjerram used Holborn's experimental results. Table I has been calculated from his smoothed curve.

† 'Roy. Soc. Proc.,' A, vol. 100, p. 367 (1921).

‡ *Loc. cit.*, p. 368.

A-three prism spectrograph with another $F/1.9$ lens showed that the aurora line was quite out of coincidence with the krypton line used for comparison, but unfortunately too long a slit was used, and the lines were too much curved for satisfactory measurement of the interval. For the rest, the three-prism instrument gave a much weaker spectrum than the other, and nothing was gained by using it.

The third instrument had a portrait lens of much smaller relative aperture, and was pointed at the sky 45° up from a southern window. An Ilford panchromatic plate was used, in the hope of getting the red part of the aurora spectrum. Nothing came out except the strongest negative band of nitrogen.

On the night of May 14 the aurora was watched visually. The moon was 7 days' old and set at 1.33 in the morning of May 15. After the moon had set, the aurora was observed high up in the north, with a variety of colours, including shades of purple and violet. It could be seen red through an orange gelatine filter, transmitting from about λ 5800. The clouds interfered considerably, no part of the sky being really clear. The form of the aurora could not be made out.

An orthochromatic plate was exposed to the sky under yellow and blue filters which were of such intensity as to give about equal actinic effects with direct moonlight, or with the light of the sky on ordinary moonless nights.* On this occasion the actinic effect under the blue filter corresponded to a more than tenfold relative intensity. Thus the auroral sky on this occasion was much richer in blue and violet rays than the ordinary night sky. The colour index was more than 2·5 units lower.

The best spectrum was that of May 14, 1921, reproduced in Plate 2, No. 1. The comparison spectrum is a krypton vacuum tube. The spectrum of May 13 was generally very similar, though not quite so intense.

The Table on p. 116 is a list of the lines and bands on the photograph, with intensities, on a scale of ten.

The whole spectrum, then, is accounted for by the chief aurora line of unknown origin, and the negative bands of nitrogen. There is nothing else on the plates except a trace of continuous spectrum, probably due to moonlight.

These plates show considerably more detail in the nitrogen bands than previous photographs. The best previous photograph, so far as I know, is that of Vegard, reproduced in 'Phys. Zeit.,' XIV, p. 680, 1913. This was taken at Bossekop, in the north of Norway, and very long exposures were given. His work had the great merit of proving beyond all doubt that the bands were really negative nitrogen bands.

* See 'Roy. Soc. Proc.,' A, vol. 99, p. 10 (1921).

		Intensity.	
		May 13.	May 14.
Green aurora line	5578	8	7
Negative nitrogen bands— Blue group	I 4709	3	2
	II 4651	3	3
	III 4599	—	2
	IV 4554	—	1 ?
Violet group	I 4278	9	9
	II 4236	5	5
	III 4199	2	4
	IV 4166	1	1 ?
Ultra-violet group	I 3914	10	10

It is remarkable that the strongest nitrogen bands are much more intense than the green aurora line, though the plates used are very sensitive in the region of the latter.

§ 2. *Laboratory Studies on this Spectrum.*

The opportunities of getting as good a photograph of the auroral spectrum as this one are few, and I was anxious to make the best use of it in determining the conditions for an artificial reproduction of the nitrogen bands exactly as they appear in the aurora. I wished, if possible, to produce them without any admixture of the various other spectra of nitrogen, but have not been wholly successful in doing so, after many attempts. Some relevant facts have, however, been gathered which are not to be found in the published literature.

A discharge tube was made as in the figure, which is one quarter size. The
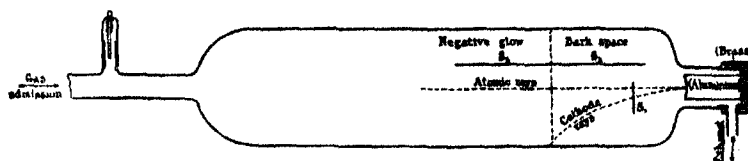
concave cathode was of aluminium, 1·2 cm. diameter, and was mounted, as shown, in a brass cap cemented with sealing-wax on to the neck of the vessel. A brass tube from the cap leads to the pump. This device was first used by Aston,* and has the great advantage of preventing a parasitic discharge from striking down to the pump through the connecting tubes. In my case it was

* 'Phil. Mag.,' vol. 39, p. 613 (1920).

not necessary to perforate the cathode, and the currents used were not heavy enough to demand water cooling. The anode was also arranged in the way used by Aston (originally by Lodge), with an insulated metal tube round it, so as to act as its own rectifier. For the rest, the figure will explain itself. A stream of rarefied air or nitrogen from a capillary inlet was passed through the tube and the rate of flow controlled by reducing the pressure in the feed reservoir. In this way the gas in the tube was kept pure and the pressure controlled. At low pressures the various features of the cathode discharge can be very well isolated in a large tube of this kind, and the spectra examined separately.

In small discharge tubes it is difficult to trace the boundary between the negative glow and dark space when the latter is much more than about 3 cm. long. The difficulty is mitigated by the use of a large tube, and still more by photography, using a filter of Wood's ultra-violet glass, which cuts off wavelengths more than about λ 4000. In this way the green luminescence of the glass, which hinders visual observation, is entirely got rid of. Such a photograph of the tube is reproduced in Plate 2, No. 7, scale natural size. The dark space is 5·6 cm. long, and the alternative spark gap between the balls about 1·3 cm.

In this photograph a weak transverse magnetic field deflects the cathode rays to the left, where they were received on a piece of mica, to avoid fracture of the glass. A pencil of undeflected rays proceeds along the axis of the tube. These are the "retrograde rays" examined by Sir J. J. Thomson.[*] He found hydrogen atoms and molecules and oxygen atoms; also negatively electrified and unelectrified atoms.

The retrograde rays in nitrogen do not seem to have been examined in detail. It will suffice to call them atomic rays in distinction from cathode (electronic) rays.

It is noteworthy that the thin pencil of cathode rays is of very small section compared with the negative glow, and that the track of these rays is as luminous in the dark space as in the negative glow, except for the superposition of the negative glow upon them. The view sometimes expressed or implied that the negative glow is simply an excitation of the gas by the pencil of cathode rays from the cathode, is seen more clearly than usual to be untenable.

The part of the discharge tube under investigation was focussed on the slit of the spectrograph, the same instrument with which the aurora was taken, but not in exactly the same adjustment as before.[†] The spectrum in Plate 2, No. 2, shows the spectrum of the dark space, which is, of course, only com-

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[*] 'Phil. Mag.,' vol. 24, p. 209 (1912).
[†] It was disturbed by an accident.

paratively dark, as a background.   Crossing it are the narrower spectra of the atomic rays and cathode rays, which are separated by the magnet, as in Plate 2, fig. 7, S_1 in the figure represents diagrammatically the position of the slit, or rather of its image.

In judging of the spectra excited by these rays, it is necessary to allow for and subtract, so to speak, the background spectrum of the dark space.

It is found that the relative intensities within the blue group of negative bands, or within the violet group, vary under different conditions of excitation.   This is most conspicuous in the blue group, where the second band may be stronger than the first.   In the violet group the first band is always much the strongest.   Accordingly, attention is concentrated on the blue group, the components of which are called I, II, III, in order of increasing refrangibility.

In the auroral spectrum of May 13 II is as strong as I.   On May 14 II was stronger than I, and III was equal to I.

Let us compare this with the artificial spectra.   In the dark space I is much stronger than II and III is barely visible.   Where the track of the cathode rays crosses the spectrum, the bands are strengthened, but their relative intensity is not conspicuously changed.   Where the atomic rays cross the spectrum II is much stronger, and III is rather stronger than I.   Thus the atomic rays give approximately the intensity ratio which obtained in the aurora of May 14.   They go slightly beyond the mark, as regards the increased relative intensity of II.

On the other hand, the dark space and the cathode rays showed no approximation to auroral conditions.

To examine the negative glow, the slit was placed parallel to the length of the discharge with its image as at $S_2 S_2$ in the figure, so that half its length was in the dark space, and half in the negative glow (Plate 2, No. 3).   The relative intensities of I, II, III, are about the same in the negative glow as in the dark space and in the cathode rays.   The negative glow is thus unlike the aurora in this regard.

There are other points of interest brought out by the photograph (Plate 2, No. 3).   The bands of the second positive group of nitrogen (see particularly those of wave-lengths 4059, 3998, 3805, 3754, which are marked with dots above the photograph) are much more strengthened in the negative glow than on the negative bands.   This behaviour of the second positive group has already been described by Seeliger and Pommeranig.[*]   On the other hand, the aluminium lines 3944 and 3962 (dotted below the photo-

* ' Ann. d. Phys.,' vol. 59, p. 595 (1919).

graph) are stronger in the dark space, which as regards these would be more correctly called a bright space.*

There is a good deal of evidence from the work of Birkeland, Stormer, and Vegard, for attributing the aurora to cathode rays from the sun. The observations which have been described do not seem very easily conformable to this view. It was thought likely that in the blue group of negative bands, II would gain intensity relative to 1 as the cathode rays became harder. I have not, however, succeeded in tracing such a tendency. A series of exposures were made at decreasing pressures, then with increasing hardness of the cathode rays, the alternative spark between balls in air varying from 0·5 mm. to 17 mm.

At 0·5 mm. alternative spark the cathode rays could not be satisfactorily observed inside the comparatively narrow dark space, as there was not room to separate them from the atomic rays. They had to be observed in the negative glow where they cross one another at the magnetically displaced focus of the concave cathode. But they are so bright at these high pressures that no ambiguity arose from this. As the alternative spark increased the dark space widened, and the cathode ray spectrum could be photographed inside it. Throughout the range from 0·5 mm. to 17 mm. the band I was much stronger than II, and no definite tendency to equalisation was noticed. At 17 mm. alternative spark it was necessary to give 5 hours' exposure, even with the great light grasp of the instruments used, and at still lower pressures the cathode beam faded into invisibility, although the atomic beam could still be traced.

Reduction of pressure has a two-fold effect. It increases the hardness of the cathode rays, and at the same time diminishes the concentration of molecules in their path. In order to examine the luminosity produced by harder rays than this, it would be necessary to control the density of the atmosphere traversed independently. This could, perhaps, be successfully done by the use of Lenard's aluminium window. It is true that by using a denser atmosphere, we should violate the conditions which obtain in the upper air. In observing the aurora we look through immense thicknesses of very feebly luminous gas. In a laboratory imitation these great thicknesses are prohibitive, and it is necessary to increase the luminosity per unit volume of the gas in some way. It may be argued that this changes the spectrum of the light, and spoils comparison with the aurora. Without a full knowledge of the mechanism of luminosity such as we do not possess at present, the criticism cannot altogether be met.

* Possibly these lines should rather be referred to the first negative layer, the limits of which are not easily defined.

So far, then, as the detailed development of the negative bands is concerned, the cathode rays do not imitate the aurora so well as the atomic rays.

The negative bands can also be observed in the "first negative layer," the luminous layer nearest the cathode, which is regarded as continuous with the canal rays, and would be prolonged into the latter if the cathode were perforated. Here, too, the negative bands have the auroral character, II, in the blue group, being equal in intensity to I (Plate 2, No. 4).

Finally, it is possible to observe the negative bands at low pressure in the capillary of a spectrum tube of the ordinary form, thus, in the positive column of the discharge. This observation is due to Hasselberg,* and was used in his measurements of the negative bands. In this case, too, the intensity distribution is like that in the aurora, the development of the later members in each group being exceptionally good. Thus, Hasselberg gives the wave-lengths of six bands in the blue group.† These bands are more like the auroral ones than any others that I have been able to produce artificially, and are shown in comparison with them in Plate 2, No. 5.

If these bands could only be obtained alone, without the second positive group, the comparison would be very satisfactory.

In the capillary at low pressures we have a procession of ions of both signs, but of opposite charges, moving in a strong electrical field.

It appears, then, that an intensity distribution like that in the aurora has not been obtained, except in cases when we can suppose the bombarding particles to be, in part at least, of atomic dimensions. Purely electronic bombardment has not been observed to give it.

This, as far as it goes, would be in favour of the idea which has sometimes been advocated, that rays from the sun of an atomic nature give rise to the aurora. I have not succeeded, however, in getting so simple a spectrum as that of Plate 2, No. 1, in any experimental bombardment of the gas with atomic rays. Let us take, for instance, the spectrum of the first negative layer. I have carefully followed the changes in the spectrum with increasing pressure.

In no case did the negative series of nitrogen bands appear without contamination with other nitrogen spectra. At the lower pressures, the nitrogen *line* 3995 was conspicuous, and of intensity comparable with the blue negative bands I and II. As the pressure increased, this line weakened, and the nitrogen bands of the second positive group, 4059, 3998,

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* 'Acad. Imp. des Sciences de St. Petersbourg,' 7th Series, vol. 32, No. 15 (1885).

† It has been suggested that the appearance of negative bands in the spectrum of the capillary is due merely to the ordinary expansion of the negative glow at low pressures. But the same effect is obtained in a specially shaped tube, in which the cathode (and anode) are both "round the corner."

3805, and 3755 came in,* but before the line had faded out. Thus, at no stage is nitrogen represented by negative bands only, as in the aurora spectrum (Plate 2, No. 1).

The best approximation to this state of things was at a dark space of 2 cm. (equivalent spark gap in air, 3 mm.). The spectrum in this case is reproduced, (Plate 2, No. 4), and shows the line 3995 marked by dots, somewhat less intense than the blue negative bands of nitrogen. The pressure is just short of that required to make the positive bands come in. I speak of the pressure because it is the independent variable which is directly observed and controlled ; but, of course, indirect and perhaps complex effects of a change of pressure are really concerned.

Again, in no case are the hydrogen lines absent from the experimental spectra. The air, or nitrogen, fed into the tube was dried with phosphorus pentoxide, though I did not specially study the effect of prolonged drying. The hydrogen appears to come from the electrode, the intensity being greatest when the electrode is new, and depending also on the material of which the latter is made. I have tried aluminium, iron, tungsten, and silicon, and experience has been in favour of the latter, which gives a minimum of hydrogen, and, moreover, gives no lines of its own. But even prolonged running of a silicon cathode does not get rid of the hydrogen lines from the first negative layer (Plate 2, No. 4).

Spectrum of the Aurora, and Composition of the Upper Atmosphere.

We have reason to believe, not indeed from direct experiment, but on very strong theoretical grounds, that the upper atmosphere in which the aurora occurs, is rich in the lightest constituents of air, helium and (possibly) hydrogen. The subject is fully discussed in a recent paper by Chapman and Milne.† Do these constituents appear in the auroral spectrum ? The photographs reproduced confirms clearly all previous evidence that they do not. We are faced, therefore, with the alternatives that either they are not there, or that the conditions of excitation are not such as to develop the spectrum.

In the case of hydrogen we have no cogent evidence that it is a normal constituent of the lower air, and we may escape from the need for explaining its absence from the aurora on this ground. On any other view a formidable difficulty would be encountered. For, according to all laboratory experience,

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* 3998 cannot be well separated from the *line* 3995 with the resolving power used, but the presence or absence of the other second positive bands mentioned serves to discriminate.

† 'J. R. Met. Soc.,' vol. 46, p. 357 (1920).

even a trace of hydrogen asserts itself in the spectrum of any kind of electric discharge through air, under any conditions of pressure.

We may turn to the question of helium, and ask whether, if present in the quantities anticipated from the theory of diffusion, it could fail to be excited by cathode ray or atomic ray bombardment of the gas. It is impossible at present to predict *a priori* the relative visibility of different gases in a mixture; indeed it depends very much on the discharge conditions. It is known that helium may be largely masked by admixture of nitrogen, but this action is most conspicuous in the positive column. To test the visibility of helium in a mixture with nitrogen, five parts of helium with one of nitrogen was fed in through a capillary tube to the large discharge vessel (figure), and the cathode ray and atomic ray spectra photographed at low pressures, the alternative spark gap between balls being held at 1 cm.

The violet and ultra-violet negative nitrogen bands are still the most conspicuous feature in both spectra (Plate 2, No. 6), but the helium lines 4471 and D_3 marked with dots above are comparable in intensity with the blue nitrogen group. In the cathode rays, these lines are scarcely, if at all, visible. On the other hand the green helium line 5016 (marked with a dot below the photograph), is weak in the atomic rays and stronger in the cathode rays, though here only about equal to the second member of the negative nitrogen group, which is comparatively weak in the cathode ray spectrum.

If diffusion in the atmosphere is considered to begin at 20 kilom. up, this composition of five volumes helium to one of nitrogen should prevail at about 130 kilom. But the particular aurora in question extended to far greater altitudes than this. Stormer[*] found for one long auroral ray heights ranging from 192 to about 470 kilom., so that the whole of this ray (the only feature about which we have published information) lay in an atmosphere which should consist almost entirely of helium. These observations were taken in the neighbourhood of Christiania. But it seems not unreasonable, considering the world-wide distribution of this aurora, to assume that it occurred at about the same height over the south of England.

We may possibly escape from the conclusion that the luminosity photographed in the spectrum (Plate 2, No. 1), occurred in an atmosphere consisting largely of helium, by putting its height near the lower limit of auroral heights (90 kilom.) and by putting the height at which separation of the gases by diffusion begins rather higher than the probable value of 20 kilom. But there is a minimum of room for escaping in this way.

[*] 'Comptes Rendus,' vol. 172, p. 1672 (1921).

Upon the whole, it appears very difficult on the hypothesis of atomic rays to explain the absence of helium lines from the spectrum and, it may be added, the absence of nitrogen line spectrum.

On the hypothesis of cathode ray excitation, this difficulty would be considerably relieved, but in that case we encounter another difficulty, namely, that the nitrogen band spectrum in the aurora has the intensity distribution characteristic of atomic rays, not of cathode rays.

It seems best at present not to lose sight of the possibility that the mode of excitation may be something entirely different from either.

§ 3. *Summary.*

A photographed spectrum of the aurora obtained on the night of March 14, 1922, is reproduced. It shows the negative bands of nitrogen in considerable detail, also the green aurora line of unknown origin, which, however, is subordinate.

A number of laboratory photographs of the negative bands of nitrogen excited in various ways are reproduced for comparison.

With atomic ray excitation, and still better in the narrow positive column (capillary tube) at low pressure the development of the negative bands can be imitated. But other nitrogen spectra (line spectrum and second positive band spectrum) persistently appear in addition.

The cathode ray spectrum is free from these foreign spectra. But the negative bands produced in this way are not developed like those in the aurora, the intensity being much more concentrated in the first band of each group. Hard and soft cathode rays behave alike in this respect.

The auroral spectrum is also discussed in relation to the upper atmosphere. Assuming that helium is the main constituent above 130 kilom., as the theory of diffusion indicates, then it is difficult, on the hypothesis of positive ray excitation, to explain its absence from the spectrum of this particular aurora, which at Christiania, reached to 470 kilom. Experiments on artificial mixtures indicate that helium should be visible.

With cathode ray excitation, this difficulty would be lessened, but the different development of the nitrogen bands remains.

It is possible that the true mode of excitation of the aurora has not yet been suggested.

DESCRIPTION OF PLATE.

No. 1.—Aurora spectrum with krypton comparison. The yellow-green aurora line,
λ 5578, is seen on the right in approximate coincidence with the strong krypton line.

No. 2.—Spectrum of nitrogen, in the cathode rays and atomic rays separately, seen on a
background of dark space, which is only relatively dark. Note the development of
the various members of the blue group in each case. The atomic rays give an
intensity distribution more like the aurora.

No. 3.—Spectrum of negative glow above (second positive group of bands marked) and
of dark space below (aluminium lines marked).

No. 4.—Spectrum of first negative layer. Nitrogen line marked.

No. 5.—Spectrum of the capillary of a nitrogen spectrum tube at low pressure, placed
in comparison with aurora. Note similar development of bands.

No. 6.—Cathode rays and positive rays in a mixture of five parts helium and one part
nitrogen. Helium lines marked.

No. 7.—Direct photograph of the discharge tube as used in obtaining spectra 2, 3, and 6.
The dark space traversed by atomic rays (straight) and cathode rays (deflected).
Below is the negative glow, then the positive column. The tube is photographed
through ultra-violet glass. Scale about one-quarter.

Fourier's Series and Analytic Functions.

By T. Carleman, Docent in Mathematics in the University of Upsala,
and G. H. Hardy, F.R.S.

1. Introduction.

1.1. In the theorems which follow we are concerned with functions $f(x)$
real for real x and integrable in the sense of Lebesgue. We do not, however,
remain in the field of the real variable, for we suppose, in §§ 4 et seq., that
$f(x)$, or a function associated with $f(x)$, is analytic, or, at any rate, harmonic,
in a region of the complex plane associated with the particular real value of x
considered.

The Fourier's series considered are those associated with the interval
$(0, 2\pi)$. If a is a point of the interval, we write

$$\phi(u) = \tfrac{1}{2}\{f(a+u)+f(a-u)-2s\} \qquad (0 < a < 2\pi), \qquad (1.11)$$

$$\phi(u) = \tfrac{1}{2}\{f(u)+f(2\pi-u)-2s\} \qquad (a = 0, a = 2\pi), \qquad (1.12)$$

where s is a constant.
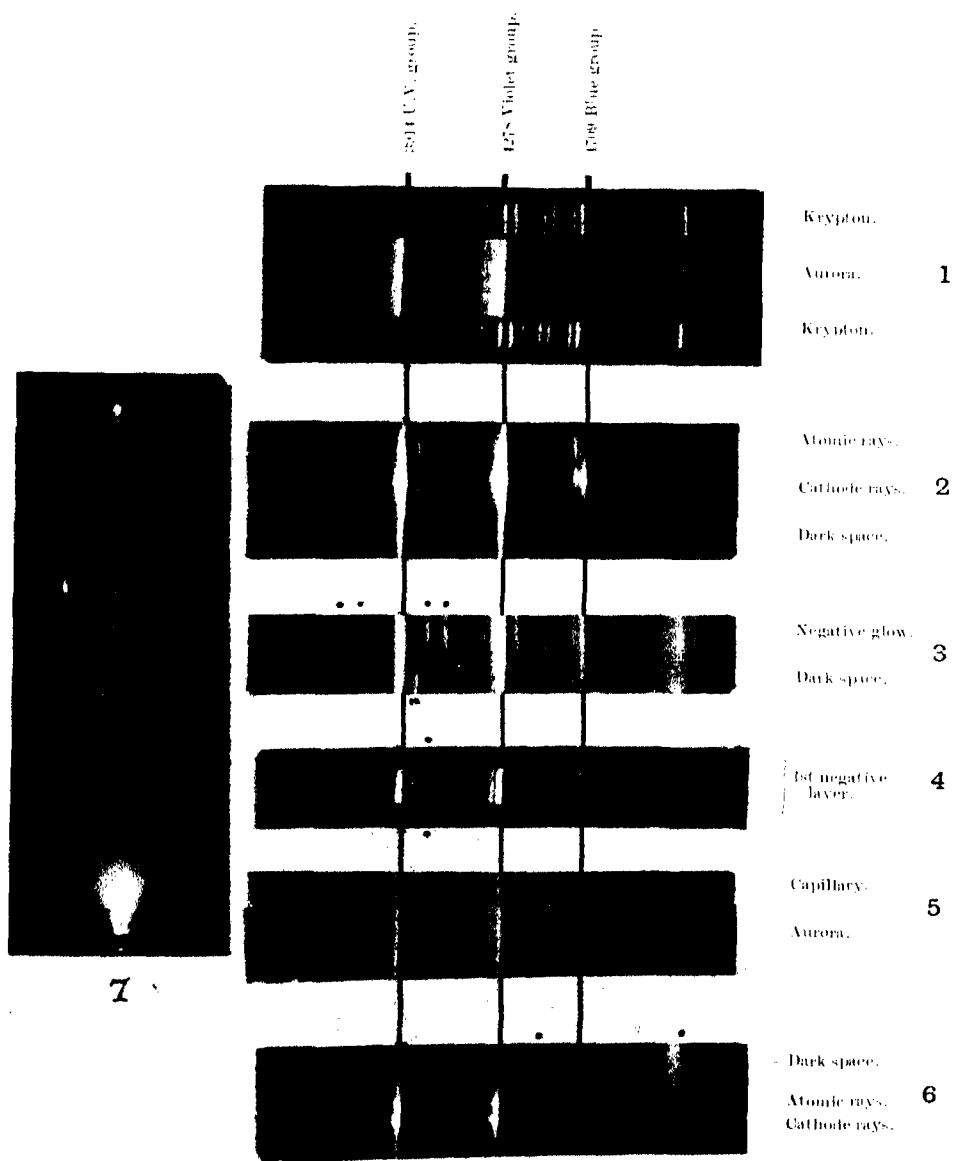
We write
$$z = x + iy, \qquad w = u + iv \qquad (1.13)$$
for the complex variables of which x and u are the real parts.

By a region Δ, or $\Delta(\delta, \alpha)$, in the plane of w, we mean a triangle defined by inequalities
$$0 \leqq R(w) \leqq \delta, \ |\arg w| \leqq \alpha \ (\delta > 0, \ 0 < \alpha \leqq \tfrac{1}{2}\pi). \qquad (1.14)$$

When we say that $\phi(w)$ is analytic (or harmonic) and bounded in Δ, we mean that it is an analytic (or harmonic) function regular at all points inside Δ, and that its modulus at all such points is less than a constant $K = K(\delta, \alpha)$. It is immaterial whether we suppose $\phi(w)$ regular at points on the boundary of Δ, other than the origin; for we can always replace Δ by a slightly smaller region of the same type. The origin is, in general, an essential singularity of $\phi(w)$.

In § 2 we prove two lemmas concerning derivatives of functions of a real variable. In § 3, remaining in the real domain, we prove a theorem concerning Fourier's series, of which our main result proves later to be a corollary. In § 4 we prove two lemmas concerning harmonic functions. In § 5 we consider our principal problem. *Given that $\phi(w)$ is harmonic and bounded in a region Δ, what is the necessary and sufficient condition that the Fourier's series of $f(x)$ should converge when $x = a$?* The answer to this question is contained in theorem 2. We also prove an analogous theorem in which, instead of supposing $\phi(w)$ bounded, we suppose that the integral
$$\iint |\phi'(w)|^2 \, du \, dv, \qquad (1.15)$$
taken over Δ, is convergent. In § 6 we add some notes relating to certain theorems of Lindelöf and Montel.

2. *Lemmas concerning derivatives of functions of a real variable.*

2.1. *Lemma* 1. *If $\psi(u)$ is a function of the real variable u, continuous and indefinitely differentiable for $0 < u < \delta$, and*
$$\psi(u) = o(1), \qquad \psi^{(p)}(u) = O\left(\frac{1}{u^p}\right), \qquad (2.12)$$
when $u \to 0$, then
$$\psi^p(u) = o\left(\frac{1}{u^p}\right). \qquad (2.13)$$

This is a special case of a known theorem.[*]

2.2. Our second lemma is of the same character, but is not actually included in any of the theorems proved in the memoir just referred to.

[*] G. H. Hardy and J. E. Littlewood, "Contributions to the Arithmetic Theory of Series," 'Proc. London Math. Soc.' (2), vol. 11, pp. 411-478, 427, Theorem 8 (1913).

Lemma 2. *Suppose that* $\psi(u)$ *is a function of the real variable* u *which possesses a third derivative* $\psi'''(u)$ *for* $0 < u < \delta$, *and that*

$$\psi(u) = o(u^2), \qquad \psi'''(u) = O\left(\frac{1}{u}\right) \tag{2.21}$$

when $u \to 0$. *Then*

$$\psi''(u) \to 0 \tag{2.22}$$

when $u \to 0$.

Let $\xi = \zeta u$, where $0 < \zeta < \frac{1}{2}$, and suppose that $0 < (1 + \zeta)u < \delta$. Then, by Taylor's Theorem,

$$\psi(u+\xi) + \psi(u-\xi) - 2\psi(u) = \xi^2\psi''(u) + \tfrac{1}{6}\xi^3\{\psi'''(u+\theta_1\xi) - \psi'''(u-\theta_2\xi)\},$$

where $0 < \theta_1 < 1, 0 < \theta_2 < 1$; and therefore

$$|\psi''(u)| \leqq \frac{1}{\xi^2}(|\phi(u+\xi)| + |\phi(u-\xi)| + 2|\phi(u)|)$$

$$+ \frac{\xi}{6}(|\psi'''(u+\theta_1\xi)| + |\psi'''(u-\theta_2\xi)|)$$

$$= \lambda + \mu, \tag{2.23}$$

say. Since $\psi'''(u) = O\left(\frac{1}{u}\right)$, we have

$$|\mu| < H\xi\left(\frac{1}{u+\theta_1\xi} + \frac{1}{u-\theta_2\xi}\right) < \frac{2H\zeta}{1-\zeta},$$

where H is a constant; and we can therefore choose ζ so that

$$|\mu| < \tfrac{1}{2}\epsilon. \tag{2.24}$$

When ζ is fixed, we have

$$\lambda = \frac{1}{\zeta^2 u^2}\{(1+\zeta)^2 o(u^2) + (1-\zeta)^2 o(u^2) + 2o(u^2)\} = o(1)$$

so that

$$|\lambda| < \tfrac{1}{2}\epsilon, \tag{2.25}$$

if u is sufficiently small. From (2.23), (2.24), and (2.25) the conclusion follows.

The form of the proof is modelled on that used by Landau in the discussion of theorems of this character.[*]

3. *Preliminary theorem.*

3.1. THEOREM 1. *Suppose that* $\phi(u)$ *possesses a second derivative* $\phi''(u)$ *for* $0 < u < \delta$, *and that*

$$\phi''(u) = O\left(\frac{1}{u^3}\right). \tag{3.11}$$

[*] See E. Landau, "Einige Ungleichungen für zweimal differentiierbare Funktionen," 'Proc. London Math. Soc.' (2), vol. 13, pp. 43–49 (1913); and 'Darstellung und Begründung einiger neuerer Ergebnisse der Funktionentheorie,' p. 54 (1916).

Then the necessary and sufficient condition that the Fourier's series of $f(x)$, for $x = a$, should converge to the sum s, is that

$$\phi(u) \to 0$$

when $u \to 0$ through positive values.

We make certain preliminary simplifications. We suppose, first, that $0 < a < 2\pi$; the modifications required when a is an end-point of the interval are trivial. We may then suppose $\delta < \mathrm{Min}\,(a, 2\pi - a)$.

We may suppose, without loss of generality, that $f = 0$, except in the interval $(a - \delta, a + \delta)$, for the behaviour of f outside this interval is irrelevant to the question of convergence. We may also suppose that $s = 0$. Thus

$$\phi(u) = \tfrac{1}{2}\{f(a+u)+f(a-u)\} \quad (0 \leqq u \leqq \delta), \quad \phi(u) = 0 \ (u > \delta). \quad (3.13)$$

If the Fourier's series of $f(x)$ is

$$f(x) \sim A_0 + \overset{\infty}{\underset{1}{\Sigma}} A_n = \tfrac{1}{2} a_0 + \overset{\infty}{\underset{1}{\Sigma}} (a_n \cos nx + b_n \sin nx), \quad (3.14)$$

then that of $\phi(u)$ is

$$\phi(u) \sim A_0 + \overset{\infty}{\underset{1}{\Sigma}} (a_n \cos na + b_n \sin na) \cos nu, \quad (3.15)$$

and the Fourier's series of $f(x)$, for $x = a$, is that of $\phi(u)$ for $u = 0$. Our problem is therefore equivalent to the corresponding problem for this latter series.

We observe that (3.11) involves

$$\phi'(u) = O\left(\frac{1}{u}\right). \quad (3.16)$$

3.21. *The condition is sufficient.* This may be proved very simply in two different ways which are each of interest.

(a) It is sufficient to prove that

$$A_n = O\left(\frac{1}{n}\right). \quad (3.21)$$

For the series is summable (C1), by the classical theorems of Fejér and Lebesgue, and a series which is summable (C1), and satisfies (3.21), is necessarily convergent.[*]

It is enough then, to prove that

$$\int_0^\delta e^{niu} \phi(u)\, du = O\left(\frac{1}{n}\right). \quad (3.22)$$

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[*] L. Fejér, "Untersuchungen über Fourier'sche Reihen," 'Math. Ann.,' vol. 58, pp. 51–69 (1904) ; H. Lebesgue, "Recherches sur la convergence des séries de Fourier," 'Math. Ann.,' vol. 61, pp. 251–280 (1905) ; G. H. Hardy, "Theorems relating to the convergence and summability of slowly oscillating series," 'Proc. London Math. Soc.,' ser. 2, vol. 8, pp. 301–320 (1909). See also Ch. J. de la Vallée Poussin, 'Cours d'analyse infinitésimale,' vol. 2, ed. 2, pp. 154–162 (1912) ; H. S. Carslaw, 'Introduction to the theory of Fourier's series and integrals,' vol. 1, ed. 2, pp. 234–243 (1921).

Since $\phi(u)$ is bounded, the integral is equal to

$$O\left(\frac{1}{n}\right) + \int_{1/n}^{\delta} e^{niu}\,\phi(u)\,du = O\left(\frac{1}{n}\right) + \left[\frac{e^{niu}\,\phi(u)}{ni}\right]_{1/n}^{\delta}$$

$$+ \left[\frac{e^{niu}\,\phi'(u)}{n^2}\right]_{1/n}^{\delta} - \frac{1}{n^2}\int_{1/n}^{\delta} e^{niu}\,\phi''(u)\,du$$

$$= O\left(\frac{1}{n}\right) + O\left(\frac{1}{n}\right) + O\left(\frac{1}{n}\right) + O\left(\frac{1}{n^2}\int_{1/n}^{\delta}\frac{du}{u^2}\right) = O\left(\frac{1}{n}\right),$$

by (3.11) and (3.16).

(b) A sufficient condition for convergence is that

$$I(\epsilon) = \int_{\epsilon}^{\delta} \frac{|\phi(u+\epsilon)-\phi(u)|}{u}\,du \to 0, \tag{3.23}$$

when $\epsilon \to 0$ by positive values.* But

$$\phi(u+\epsilon)-\phi(u) = \epsilon\phi'(u+\theta\epsilon) \quad (0 < \theta < 1)$$

and

$$\phi'(u) = o\left(\frac{1}{u}\right),$$

by Lemma 1. Hence

$$I(\epsilon) = o\left(\epsilon\int_{\epsilon}^{\delta}\frac{du}{u(u+\theta\epsilon)}\right) = o\left(\epsilon\int_{\epsilon}^{\delta}\frac{du}{u^2}\right) = o(1),$$

which proves (3.23).

3.3. *The condition is necessary.* We denote by $\Phi(u)$ Riemann's function

$$\Phi(u) = \tfrac{1}{2}A_0 u^2 + \sum_{1}^{\infty}\frac{A_n}{n^2}(1-\cos nu) \quad (0 < u < \delta), \tag{3.31}$$

and by $\phi_2(u)$ the function

$$\phi_2(u) = \int_0^u dy \int_0^y \phi(t)\,dt \quad (0 < u < \delta), \tag{3.32}$$

These two functions are identical. For the Fourier's series of $\phi(u)$ is convergent when $0 < u < \delta$, since $\phi(u)$ has a second derivative for such values of u, and therefore† $\Phi(u)$ has, for such values of u, a generalised second derivative equal to $\phi(u)$. But $\phi_2(u)$ has an ordinary second derivative, and *a fortiori* a generalised second derivative, also equal to $\phi(u)$. Hence

$$\Psi(u) = \Phi(u) - \phi_2(u)$$

has, for such values of u, a generalised second derivative which is everwhere zero; and is therefore‡ a linear function $C + Du$. If now the series is

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* H. Lebesgue, *loc. cit.*, p. 263, and ' Leçons sur les séries trigonométriques,' pp. 59, 64 ; Ch. J. de la Vallée Poussin, *loc. cit.*, p. 150.

† By ' Riemann's First Theorem,' De la Vallée Poussin, *loc. cit.*, p. 172.

‡ By ' Schwarz's Lemma,' De la Vallée Poussin, *loc. cit.*, p. 171.

convergent for $u = 0$, we have* $\Phi(u) = o(u^2) = o(u)$, and it is evident from (3.32) that $\phi_2(u) = o(u)$. Hence $C + Du = o(u)$, which is only possible if $C = D = 0$. Thus $\phi_2(u) = \Phi(u)$, and so

$$\phi_2(u) = o(u^2). \tag{3.33}$$

Also
$$\phi_2'''(u) = \phi'(u) = O\left(\frac{1}{u}\right), \tag{3.34}$$

by (3.16). From (3.33) and (3.34) it follows, by Lemma 2, that

$$\phi_2''(u) = \phi(u) = o(1),$$

which completes the proof of the theorem.

4. *Lemmas concerning harmonic functions.*

4.1. *Lemma* 3.—*Suppose that* $u(x, y) = u(r, \theta)$ *is a real harmonic function regular for* $r < R$, *and that*

$$|u| < M \qquad (r \leqq R). \tag{4.11}$$

Then

$$\left| \left(\frac{\partial^{p+q} u}{\partial^p x \, \partial^q y} \right)_0 \right| \leqq \frac{2(p+q)! \, M}{R^{p+q}}, \tag{4.12}$$

the suffix indicating a value taken at the origin.

We have, by the familiar formula of Poisson,

$$u(x, y) = \frac{1}{2\pi} \int_0^{2\pi} \frac{R^2 - r^2}{R^2 - 2Rr \cos(\phi - \theta) + r^2} \, u(R, \phi) \, d\phi$$

$$= \frac{1}{2\pi} \int_0^{2\pi} \left\{ \frac{R}{R - e^{i\phi}(x - iy)} + \frac{R}{R - e^{-i\phi}(x + iy)} - 1 \right\} u(R, \phi) \, d\phi.$$

Hence

$$\left(\frac{\partial^{p+q} u}{\partial^p x \, \partial^q y} \right)_0 = \frac{(p+q)!}{2\pi R^{p+q}} \int_0^{2\pi} \left\{ (-i)^q e^{(p+q)i\phi} + i^q e^{-(p+q)i\phi} \right\} u(R, \phi) \, d\phi,$$

and the result follows immediately.

4.2. *Lemma* 4.—*Suppose that* $\phi(w)$ *is harmonic and bounded in a region* Δ. *Then*

$$\phi^{(p)}(u) = \left(\frac{d}{du} \right)^p \phi(u) = O\left(\frac{1}{u^p}\right) \tag{4.21}$$

when $u \to 0$ *by positive values.*

Let ξ be a small real value of w, and $R = \xi \sin \alpha$ the perpendicular from $w = \xi$ on to one of the sides of Δ through $w = 0$. The circle whose centre is $w = \xi$, and whose radius is R, lies entirely inside Δ if ξ is sufficiently small. Applying lemma 3, with $q = 0$, we obtain

$$\phi^{(p)}(\xi) = O\left(\frac{1}{R^p}\right) = O\left(\frac{1}{\xi^p}\right),$$

which proves the lemma.

* Again by ' Riemann's First Theorem.'

5. *Proof of the main theorems.*

5.1. THEOREM 2.—*Suppose that $\phi(w)$ is harmonic and bounded in a region Δ. Then the necessary and sufficient condition that the Fourier series of $f(x)$, for $x = a$, should be convergent, is that $\phi(u) \to 0$ when $u \to 0$ through positive values.*

By Lemma 4, $\phi''(u) = O\left(\dfrac{1}{u^2}\right)$. The theorem is thus an immediate corollary of Theorem 1.

As a special case we have,

THEOREM 3.—*If $\phi(u)$ is the value, when $u = 0$, of the real component of a function $F(w)$ of the complex variable w, and $F(w)$ is analytic and bounded in a region Δ, then the necessary and sufficient condition for convergence is that $\phi(u) \to 0$.*

This is the form in which we originally proved the theorem. The idea of extending it to any bounded harmonic function was suggested to us by Dr. Marcel Riesz.

5.2. We next prove a theorem which resembles Theorem 3 in all respects save one. We omit the condition that $F(w)$ is *bounded* in Δ, substituting for this the condition that the integral (1.15) should be convergent. The condition has a simple geometrical meaning, namely that Δ is mapped, by the transformation $W = F(w)$, on a region of finite area in the plane of W.

THEOREM 4. *Suppose that $\phi(u) = \phi(u, 0)$ is the value, for $v = 0$, of the real part $\phi(u, v)$ of a function $F(w)$ analytic in Δ, and that the integral (1.15) is convergent. Then the necessary and sufficient condition that the Fourier's series of $f(x)$, for $x = a$, should converge to the sum s, is that $\phi(u) \to 0$ when $u \to 0$ through positive values.*[*]

We have our proof of Theorem 4 on the following additional lemma.

5.2. *Lemma* 5.—*If $F(w)$ is analytic in Δ, and the integral (1.15) is convergent, then*

$$F^{(n)}(w) = o\left(\frac{1}{w^n}\right) \tag{5.21}$$

when $w \to 0$ in any manner inside a region Δ' interior to Δ. In particular

$$\phi^{(n)}(u) = o\left(\frac{1}{u^n}\right) \tag{5.22}$$

when $u \to 0$ through positive values.

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[*] It may be well to point out explicitly that the convergence of (1.15) does not in itself imply the boundedness of $F(w)$ in Δ. A simple example to the contrary is obtained by taking $F(w) = \log\log w$. An example in which $F(w)$ is bounded, but (1.15) is not convergent, is given by $F(w) = w^{ci}$, where c is positive. The integral (1.15) is equal to either of the integrals

$$\iint (\phi_u^2 + \phi_v^2)\, du\, dv, \quad \iint (\psi_u^2 + \psi_v^2)\, du\, dv,$$

where $\phi + i\psi = F$. There is therefore no theorem more general than 4 and related to 4 as 2 is to 3.

We require (5.21) only when w is real, and state our proof for this case. The modifications necessary in the general case are trivial and may be left to the reader.

Suppose then that u is real, and that C is the circle whose centre is $w = u$ and which touches the oblique sides of Δ. The radius of C is $\rho = u \sin \alpha$, and we have

$$F(w) = \sum_{0}^{\infty} \frac{F^{(n)}(u)}{n!} (w - u)^n = \sum_{0}^{\infty} \alpha_n (w - u)^n \qquad (5.23)$$

for $|w - u| < \rho$. Also

$$\sum_{n=1}^{\infty} n |\alpha_n|^2 \rho^{2n} = \frac{1}{\pi} \iint |F'(w)|^2 \, du \, dv, \qquad (5.24)$$

the integration now being over the interior of C.[*] This integral tends to zero when $u \to 0$, since (1.15) is convergent. Hence

$$n |\alpha_n|^2 \rho^{2n} = \frac{n}{(n!)^2} |F^{(n)}(u)|^2 (u \sin \alpha)^{2n} = o(1), \qquad (5.25)$$

or

$$F^{(n)}(u) = o\left(\frac{1}{u^n}\right);$$

which proves (5.21), for real w, and *a fortiori* (5.22).

5.23. The proof of Theorem 4 is now immediate. We have only to take $n = 2$ in (5.22), and the theorem becomes a corollary of Theorem 1.

Note on certain theorems of Lindelöf and Montel.

6.1. We were originally led to Theorem 2 by an argument which differs materially, as regards the proof of the *necessity* of (3.12), from that of § 3. Our original argument depended upon a very interesting theorem first proved by Montel.[†] This theorem, in its simplest form, may be stated as follows :—

Suppose that (i) $\phi(w)$ *is analytic and bounded in a region* Δ, *and* (ii) *that* $\phi(w) \to 0$ *when* $w \to 0$ *by positive values. Then* $\phi(w) \to 0$ *uniformly, when* $w \to 0$ *in any manner within any region* Δ' *interior to* Δ.

This theorem has been generalised by Montel himself and by Lindelöf,[‡] in

* See L. Fejér, " Über die Konvergenz der Potenzreihe an der Konvergenzgrenze in Fällen der konformen Abbildung auf die schlichte Ebene," ' H. A. Schwarz Festschrift,' pp. 42–53 (47), (1914).

† P. Montel, " Sur les familles de fonctions analytiques qui admettent des valeurs exceptionnelles dans un domaine," ' Annales Scientifiques de l'École Normale Supérieure,' (3), vol. 29, pp. 487–535 (519), (1912).

‡ E. Lindelöf, " Sur un principe général de l'analyse," ' Acta Soc. Fennicæ,' vol. 46, no. 4, pp. 1–35 (7), (1915). A different proof of what is substantially the theorem proved here by Lindelöf was given later by Hardy and Littlewood (" Abel's Theorem and its converse," ' Proc. London Math. Soc.,' ser. 2, vol. 18, pp. 205–235 (p. 218, lemma ϵ). (1917).

two directions. In the first place the hypothesis (i) may be replaced by the more general hypothesis that $\phi(w)$ does not assume either of two exceptional values. Secondly, we may consider, instead of the straight line of hypothesis (ii), any simple continuous path which leads to the origin from inside Δ.

We are concerned here only with the theorem in its simplest form. It seems worth while to point out how naturally it follows from some of the lemmas on which our preceding analysis depends.

Suppose that $|\phi(w)| < M$ in Δ and that u is real. Then, if C is the circle of § 4.2, we have

$$|\phi^{(n)}(u)| = \left| \frac{n!}{2\pi i} \int_C \frac{\phi(w)}{(w-u)^{n+1}} \right| \leqq \frac{n!\,M}{(u\sin\alpha)^n}. \tag{6.11}$$

Thus $\phi(u) = o(1), \qquad \phi^{(n)}(u) = O\left(\frac{1}{u^n}\right),$

for every n, and therefore, by Lemma 1,

$$\phi^{(n)}(u) = o\left(\frac{1}{u^n}\right). \tag{6.12}$$

Now let $\alpha' < \alpha$ be the angle of Δ' corresponding to α, and C' the circle of radius $u\sin\alpha'$ corresponding to C. If w lies within C' we have

$$\phi(w) = \sum_0^\infty \frac{\phi^{(n)}(u)}{n!}(w-u)^n = \sum_0^p + \sum_{p+1}^\infty = \phi_1 + \phi_2, \tag{6.13}$$

say. From (6.11) we deduce

$$|\phi_2| \leqq \sum_{p+1}^\infty \frac{1}{n!} \cdot \frac{n!\,M}{(u\sin\alpha)^n} \cdot (u\sin\alpha')^n = M\left(\frac{\sin\alpha'}{\sin\alpha}\right)^{p+1} \frac{\sin\alpha}{\sin\alpha - \sin\alpha'},$$

which tends to zero when $p \to \infty$. We have therefore

$$|\phi_2| < \tfrac{1}{2}\epsilon \tag{6.14}$$

if only p is sufficiently large. When p is fixed, every term of ϕ_1 is of the form

$$o\left(\frac{1}{u^n}\right) O(u^n) = o(1)$$

in virtue of (6.12), so that

$$|\phi_1| < \tfrac{1}{2}\epsilon \tag{6.15}$$

if u is sufficiently small. From (6.13), (6.14), and (6.15) the conclusion follows.

6.2. The direct analogue of Montel's theorem for *harmonic* functions is false, as appears at once from the trivial example $\phi = \arctan(v/u)$. A modification of the argument of 6.1 leads, however, to the following result:—

Suppose that $\phi(u, v)$ is a real harmonic function, regular and bounded in Δ,

and that $\phi \to 0$ when $w \to 0$ along either of two radii vectores interior to Δ. Then $\phi \to 0$ uniformly when $w \to 0$ in any manner within any region Δ' interior to Δ.

6.3. Similar arguments, based upon Lemma 5, lead to the conclusion that *in Montel's theorem of* 6.1, *the hypothesis that $\phi(w)$ is bounded may be replaced by the hypothesis that the integral* (1.15) *is convergent.* A direct proof of this theorem is not without interest, but the actual result is included in the more general theorems referred to in 6.1.*

On the Free Transverse Vibrations of a Uniform Circular Disc Clamped at its Centre; and on the Effects of Rotation.

By R. V. SOUTHWELL, M.A.

INTRODUCTION AND SUMMARY.

§ 1. A thin circular disc, entirely unconstrained, can vibrate transversely in modes which may be characterized by any number of nodal concentric circles, crossed by uniformly spaced nodal diameters. The natural frequencies, for a disc of uniform thickness, have been calculated by Kirchhoff,[†] and a recent investigation by Prof. Lamb and the present author[‡] has shown the amount by which they are increased when the disc rotates at any given speed about its axis.

This extension of Kirchhoff's analysis was suggested by published accounts of failures in turbine discs, the circumstances of which indicated that they had their origin in forced vibrations, intensified by resonance.[§] It was realised that the results would be only indirectly applicable to design, mainly because in practice discs are constructed with curved profiles (the thickness increasing from the rim to the boss), but also because the calculated

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* For $\phi(w)$ covers a finite area when w covers Δ, and there are therefore infinitely many values which $\phi(w)$ does not take.

† "Ueber die Schwingungen einer elastischen Scheibe," 'Crelle's Journal,' vol. 40 (1850), and 'Pogg. Ann.,' vol. 81 (1850). The essentials of the analysis are reproduced in Lord Rayleigh's 'Theory of Sound,' vol. 1, §§ 218, 219.

‡ 'Roy. Soc. Proc.,' A, vol. 99, pp. 272–280 (1921). Throughout the present investigation this paper will be quoted by the abbreviated title "Spinning Discs," and its equations by their number with an A affixed : thus equation (34A) below is equation (34) of the "Spinning Discs" paper.

§ *Cf.* K. Baumann, "Some Recent Developments in Large Steam Turbine Practice," 'Journ. Inst. Elect. Eng.,' vol. 59, pp. 619, 620 (1921).

frequencies, in some instances, will be seriously affected by the "clamping" which is introduced when the disc is attached at its centre to a shaft and rotor of considerable inertia.

Varying thickness, and the allied complication of loads imposed at the rim by the inertia of the blading, introduce difficulties of such magnitude that it will probably not be possible to calculate the effects of these factors with any great accuracy. But the effect of central clamping may be studied in a general fashion, if we confine our attention, as before, to a disc of uniform thickness, and calculate, by a further extension of Kirchhoff's analysis, the increase in frequency which results when a constraint of this nature is introduced. The present paper contains the results of an investigation on these lines. Its scheme is generally similar to that of the joint paper to which reference has been made; that is to say, exact calculations are given for the two limiting cases obtained by neglecting in turn the centrifugal and the flexural stress-systems, and these are followed by an approximate treatment of the problem in its general form.

The assumption made in regard to "central clamping," requires some explanation. It is evident that in practice any alteration in the dimensions of the boss will modify not only the boundary conditions imposed upon the transverse displacement, but also the centrifugal stress-system, which in part determines the differential equation governing this displacement at all points in the disc. Both of these effects will influence the natural frequencies of vibration, the first in a way which we may regard as direct, and the second indirectly. Now the centrifugal stress-system, in practice, will depend upon many factors (*e.g.*, the diameter of the boss, the diameter of the shaft, the stresses imposed by the process of "shrinking on," the weight of the blading, etc.), and it is not possible to make any one assumption in regard to its distribution which will satisfactorily represent all cases. For the purpose of the present paper, which is intended to throw light on the general principles involved, it has therefore been thought best to concentrate attention upon the *direct* consequences of clamping, and to assume that the clamps prevent transverse displacement without altering the centrifugal system, so that this system is such as obtains in a disc which is continuous up to the centre.

A constraint of this nature is easily visualized (*e.g.*, clamps which are brought into contact with the rotating disc *after it has taken up the strains appropriate to its speed of rotation*), and it is easy to reproduce in experiments. The approximate methods given in the concluding section of this paper enable us to deal with any other system of centrifugal stresses which may be specified, and in our exact calculations (§ 3) for the spinning membrane (or

disc of negligible flexural rigidity), by retaining unchanged the differential equation used previously, we are led to the interesting conclusion that in this limiting case clamping has no direct effect upon the frequencies, although it alters the modes by introducing terms which would become infinite at the centre ; it follows that the only way in which clamps can modify the frequencies is indirectly, by changing the centrifugal stress-system.

The other limiting case, of the non-rotating disc, is discussed in § 2. Figs. 3–6 show how the frequency varies with the radius of clamping in the gravest modes having 0, 1, 2 or 3 nodal diameters, and some of the higher frequencies have been calculated for the special case in which the radius of the clamping circle is infinitesimal. It was to be expected that a constraint of this particular type would involve no alteration in frequency for modes having two or more nodal diameters, since in such modes both the displacement and the slope vanish at the centre even when the disc is completely free. It is also found, somewhat unexpectedly, to be without effect in modes having one nodal diameter,* although the frequency in the gravest mode rises very rapidly with an increase in the radius of the clamping circle ; but for the "symmetrical" modes, in which there are no nodal diameters, an entirely new series of frequencies is obtained when the centre of the disc is clamped.

In the general case, when the flexural and centrifugal systems are both operative, the conclusion is reached that clamping confined to a small circle has a negligible influence upon the gravest frequencies in modes which have two or more nodal diameters, and that sufficiently exact estimates of these frequencies can be obtained, as explained in the "Spinning Discs" paper, from the relation

$$p^2 = p_1{}^2 + p_2{}^2, \qquad (34\text{A})$$

where p_1 and p_2 are the gravest values of p found by neglecting (1) the flexural rigidity and (2) the rotation. This formula gives an estimate which is of the nature of a *lower limit* to the true value. It also yields reasonably accurate results as applied to modes having one nodal diameter, if p_2 is given the value appropriate to the size of clamping circle considered. But in the symmetrical modes the gravest frequency found by neglecting the flexural rigidity is zero, the effect of the central constraint being *nil*; hence, the formula (34A), as applied to this case, would make no allowance for the effect of rotation. It is evident that the flexural rigidity, in a disc of which the centre is clamped, must in practice prevent the occurrence of modes in which the displacement, or its slope, is discontinuous at the centre, and will in this way bring the centrifugal system into operation. Special calculations are therefore required for the symmetrical modes, and the gravest frequency has

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* In these, $\partial w/\partial r$ has finite values at the centre when the disc is completely free.

been investigated (Section II b, § 5) by means of Rayleigh's method of an assumed type,* in which the potential and kinetic energies are calculated on the basis of an assumed form of w, and the frequencies determined from the condition that their sum must be constant in the vibration. It is known that this method gives an upper limit to the true value, and hence it may also be applied to modes having nodal diameters, as a convenient means of estimating the limits of possible error involved in the use of the formula (34A).

Although it still has no direct bearing on the occurrences in actual turbine discs, it is evident that our analysis has been made more representative of practical conditions by the assumption of central clamping. The new frequencies found for the symmetrical modes are of special interest, since it appears that vibrations of this type have been a source of trouble in practice.†

Exception may perhaps be taken to the fact that in this, as in the former paper, certain factors which would require consideration in a strict theory of flexure have been ignored: no account has been taken of the additional deflections which accompany the transverse shear stresses, or of the terms which depend on "rotatory inertia." Both of these factors increase in importance with the thickness of the disc, and occur whether the disc rotates or not. In the latter case they are generally neglected, and are in fact quite unimportant except in the higher modes of vibration, where the disc is divided by nodal lines into a large number of segments. When the disc rotates, the terms which depend upon "rotatory inertia" are modified by the addition of terms of "gyroscopic" type, containing the angular velocity ω as a factor. It is not difficult to show that these cancel out of the general differential equation of transverse vibration, but they appear in the boundary conditions. On the other hand, in the problems of this and the former paper they prove to be of the same order of magnitude as the other "rotatory inertia" terms (of ordinary type), and may therefore be equally neglected.

The author desires to acknowledge his indebtedness to Miss B. S. Gough and Miss S. W. Skan, of the Aeronautics Department, National Physical Laboratory, for the valuable assistance they have given him in the detailed calculations of this paper; also to Miss C. G. C. Phillips, who prepared the diagrams for reproduction.

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* 'Theory of Sound,' vol. 1, §§ 88, 89.

† *Cf.* Baumann, *loc. cit.*

I. Free Transverse Vibrations of a Non-Rotating Circular Disc Clamped at its Centre.

§ 2. Following Kirchhoff and Rayleigh, we shall neglect the effects of " rotatory inertia" and of the additional deflection caused by shear. Then the differential equation which governs the transverse displacement (w) of the middle-surface may be written, in polar co-ordinates, as follows[*] :—

$$\rho \frac{\partial^2 w}{\partial t^2} + \frac{Eh^2}{3(1-\sigma^2)} \left[\frac{\partial^2}{\partial r^2} + \frac{1}{r} \frac{\partial}{\partial r} + \frac{1}{r^2} \frac{\partial^2}{\partial \theta^2} \right]^2 w = 0. \tag{1}$$

In this equation, ρ denotes the density of the material, E Young's Modulus, and σ Poisson's Ratio, while h is the half-thickness of the plate.

The boundary conditions of the present problem are

$$\left. \begin{array}{l} \dfrac{\partial^2 w}{\partial r^2} + \sigma \left(\dfrac{1}{r} \dfrac{\partial w}{\partial r} + \dfrac{1}{r^2} \dfrac{\partial^2 w}{\partial \theta^2} \right) = 0, \\[3mm] \dfrac{\partial}{\partial r} \left[\dfrac{\partial^2 w}{\partial r^2} + \dfrac{1}{r} \dfrac{\partial w}{\partial r} + \dfrac{1}{r^2} \dfrac{\partial^2 w}{\partial \theta^2} \right] + \dfrac{(1-\sigma)}{r^2} \dfrac{\partial^2}{\partial \theta^2} \left[\dfrac{\partial w}{\partial r} - \dfrac{w}{r} \right] = 0, \end{array} \right\} \tag{2}$$

at the free edge ($r = a$), and

$$\left. \begin{array}{l} w = 0, \\[2mm] \dfrac{\partial w}{\partial r} = 0, \end{array} \right\} \text{ at the circumference of the clamping circle } (r = b). \tag{3}$$

Assuming a solution of the type

$$w = W \sin s\,(\theta - \theta_0) \sin p\,(t - t_0), \tag{4}$$

and substituting in (1), we obtain the equation

$$\left[\frac{d^2}{dr^2} + \frac{1}{r} \frac{d}{dr} - \frac{s^2}{r^2} \right]^2 W - \kappa^4 W = 0, \tag{5}$$

where

$$\kappa^4 = \frac{3(1-\sigma^2)\rho p^2}{Eh^2}. \tag{6}$$

The complete expression for W thus consists of the two solutions of the equation

$$\left[\frac{d^2}{dr^2} + \frac{1}{r} \frac{d}{dr} - \frac{s^2}{r^2} + \kappa^2 \right] W = 0, \tag{7}$$

together with the two solutions of the equation

$$\left[\frac{d^2}{dr^2} + \frac{1}{r} \frac{d}{dr} - \frac{s^2}{r^2} - \kappa^2 \right] W = 0. \tag{8}$$

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[*] *Cf.* Rayleigh, 'Theory of Sound,' vol. 1, §218, or Love, 'Theory of Elasticity,' § 314 (d).

The solutions of (7) are the Bessel functions denoted by $J_s(\kappa r)$ and $Y_s(\kappa r)$, and the solutions of (8) are the modified Bessel functions denoted by $I_s(\kappa r)$ and $K_s(\kappa r)$. Thus we have

$$W = \alpha J_s(\kappa r) + \beta Y_s(\kappa r) + \gamma I_s(\kappa r) + \delta K_s(\kappa r), \tag{9}$$

where α, β, γ and δ are arbitrary coefficients.

Then if we employ the recurrence formulæ for Bessel functions, viz.,

$$\left. \begin{array}{l} J_n'(z) = \dfrac{n}{z} J_n(z) - J_{n+1}(z), \\[2mm] I_n'(z) = \dfrac{n}{z} I_n(z) + I_{n+1}(z), \end{array} \right\} . \tag{10}$$

and the similar formulæ for $Y_n'(z)$ and $K_n'(z)$ respectively,* the edge conditions (2) may be written in the form†

$$\kappa^2 \Bigg(\alpha \left[J_s(\kappa a) - (1-\sigma) \left\{ \frac{s(s-1)}{\kappa^2 a^2} J_s(\kappa a) + \frac{1}{\kappa a} J_{s+1}(\kappa a) \right\} \right]$$

$$+ \beta \left[Y_s(\kappa a) - (1-\sigma) \left\{ \frac{s(s-1)}{\kappa^2 a^2} Y_s(\kappa a) + \frac{1}{\kappa a} Y_{s+1}(\kappa a) \right\} \right]$$

$$- \gamma \left[I_s(\kappa a) + (1-\sigma) \left\{ \frac{s(s-1)}{\kappa^2 a^2} I_s(\kappa a) - \frac{1}{\kappa a} I_{s+1}(\kappa a) \right\} \right]$$

$$- \delta \left[K_s(\kappa a) + (1-\sigma) \left\{ \frac{s(s-1)}{\kappa^2 a^2} K_s(\kappa a) - \frac{1}{\kappa a} K_{s+1}(\kappa a) \right\} \right] \Bigg) = 0 \tag{11}$$

and

$$\kappa^2 \Bigg(\alpha \left[s J_s(\kappa a) - \kappa a J_{s+1}(\kappa a) + \frac{(1-\sigma) s^2}{\kappa^2 a^2} \left\{ (s-1) J_s(\kappa a) - \kappa a J_{s+1}(\kappa a) \right\} \right]$$

$$+ \beta \left[s Y_s(\kappa a) - \kappa a Y_{s+1}(\kappa a) + \frac{(1-\sigma) s^2}{\kappa^2 a^2} \left\{ (s-1) Y_s(\kappa a) - \kappa a Y_{s+1}(\kappa a) \right\} \right]$$

$$- \gamma \left[s I_s(\kappa a) + \kappa a I_{s+1}(\kappa a) - \frac{(1-\sigma) s^2}{\kappa^2 a^2} \left\{ (s-1) I_s(\kappa a) + \kappa a I_{s+1}(\kappa a) \right\} \right]$$

$$- \delta \left[s K_s(\kappa a) + \kappa a K_{s+1}(\kappa a) - \frac{(1-\sigma) s^2}{\kappa^2 a^2} \left\{ (s-1) K_s(\kappa a) \right. \right.$$

$$\left. \left. + \kappa a K_{s+1}(\kappa a) \right\} \right] \Bigg) = 0, \tag{12}$$

---

* Whittaker and Watson, 'Modern Analysis,' §§ 17.21, 17.61, 17.7, and 17.71.

† The coefficients κ and κ^2 are important, since the equations may be satisfied solely by reason of κ being zero : a being necessarily finite, equation (12) has been multiplied throughout by this quantity.

whilst the conditions (3) at the circumference of the clamping circle become

$$\alpha J_s(\kappa b) + \beta Y_s(\kappa b) + \gamma I_s(\kappa b) + \delta K_s(\kappa b) = 0 \qquad (13)$$

and

$$\kappa \left\{ \alpha \left[\frac{s}{\kappa b} J_s(\kappa b) - J_{s+1}(\kappa b) \right] + \beta \left[\frac{s}{\kappa b} Y_s(\kappa b) - Y_{s+1}(\kappa b) \right] \right.$$

$$\left. + \gamma \left[\frac{s}{\kappa b} I_s(\kappa b) + I_{s+1}(\kappa b) \right] + \delta \left[\frac{s}{\kappa b} K_s(\kappa b) + K_{s+1}(\kappa b) \right] \right\} = 0. \quad (14)$$

Eliminating the coefficients α, β, γ, δ from (11)—(14), we obtain a determinantal equation which, for any required value of the ratio b/a, may be solved by trial,* assumed values of κa being adopted, and the resulting values of the determinant plotted against these. Table I gives results obtained in this way in respect of the gravest frequencies for modes in which s has the values 0, 1, 2 and 3 : σ has been taken to be 0·3.

Table I.

$s = 0.$		$s = 1.$		$s = 2.$		$s = 3.$	
$b/a.$	$\kappa a.$	$b/a.$	$\kappa a.$	$b/a.$	$\kappa a.$	$b/a.$	$\kappa a.$
0·276	2·50	0·060	1·68	0·186	2·50	0·43	4·0
0·642	5·00	0·397	3·00	0·349	3·00	0·59	5·0
0·840	9·00	0·603	4·60	0·522	4·00	0·71	7·0
		0·634	5·00	0·769	8·00	0·82	10·0
		0·771	8·00	0·81	10·00		
		0·827	11·00				

In the limiting case, when the radius of the clamping circle is indefinitely reduced, the analysis may be considerably simplified. For if s has a value greater than 1, the coefficients of α and β in (13) and (14) vanish when $b = 0$, and these relations will accordingly be satisfied by making γ and δ zero, without restriction of α or β. The frequencies are thus found by eliminating α and β between (11) and (12), which now reduce to the corresponding equations of Kirchhoff for a completely free disc.

* Tables of the functions $J_n(z)$ and $I_n(z)$ (n integral) are given by Gray and Matthews, 'Treatise on Bessel Functions,' pp. 247–288. The Neumann functions $Y_0(z)$ and $Y_1(z)$, as here defined, have been tabulated by the British Association, 'Report for 1914,' pp. 75–82, and the functions $K_0(z)$ and $K_1(z)$ by W. S. Aldis, 'Roy. Soc. Proc.,' A, vol. 64, pp. 203–223 (1899).

When s has the values 1 or 0, we may substitute in (13) and (14) from the ascending series for the Bessel functions.   We have

$$J_0(z) = 1 - \frac{z^2}{4} + \ldots, \qquad J_1(z) = \frac{z}{2} - \frac{z^3}{16} + \ldots,$$

$$I_0(z) = 1 + \frac{z^2}{4} + \ldots, \qquad I_1(z) = \frac{z}{2} + \frac{z^3}{16} + \ldots,$$

$$Y_0(z) = J_0(z) \log z + \frac{z^2}{4} + \ldots,$$

$$Y_1(z) = J_1(z) \log z - \frac{1}{z} - \frac{z}{4} + z^3 \ldots,$$

$$K_0(z) = -I_0(z)\{\log z - E\} + \frac{z^2}{4} + \ldots,$$

$$K_1(z) = -I_1(z)\{\log z - E\} - \frac{1}{z} + \frac{z}{4} + \ldots,$$

$$\tag{15}$$

where* $E = \log 2 - \gamma$ (γ being Euler's constant),
$$= 0.11593\ldots$$

Hence (observing that the limit of $z \log z$, when $z \to 0$, is zero) we see that the significant terms in (13) and (14), when $s = 1$, are

$$-\frac{1}{\kappa b}(\beta + \delta) = 0,$$

and
$$\frac{\alpha + \gamma}{2} + \beta \left(\frac{\log \kappa b}{2} + \frac{1}{\kappa^2 b^2} + \frac{1}{4}\right) - \delta \left(\frac{\log \kappa b - E}{2} - \frac{1}{\kappa^2 b^2} + \frac{1}{4}\right) = 0,$$

$$\tag{16}$$

respectively.   It follows that $(\beta + \delta)$ must vanish, and that both β and δ must be infinitesimal in comparison with α and γ, although their contribution to the value of the *slope* is finite at the centre.   Hence, if κa is finite, the contributions of β and δ to (11) and (12) will be infinitesimal, and the finite frequencies of vibration in modes characterized by one nodal diameter can be found from a relation identical with that which obtains for a completely free disc; that is to say, these frequencies also are unaffected by clamping which is entirely confined to the centre.

The gravest frequency for the completely free disc, in modes characterized by one nodal diameter, is zero, the "vibration" consisting simply in a rigid-body rotation of the disc about a diameter.   We should expect that this zero frequency will become finite when the slope of the disc is constrained at the centre; but it is easily verified that equations (11)—(14), when $s = 1$, are satisfied if we write

$$\kappa a = \kappa b = 0,$$

* This significance for E (the symbol employed in the tables referred to) continues down to equation (24), after which E is again used to denote Young's Modulus.

so that a zero frequency of vibration is still possible in the limiting case, when the radius of the clamping circle is indefinitely reduced. Alternatively, the existence of a mode having zero frequency can be established by verifying that the expression

$$w = (\epsilon r + \zeta r \log r) \sin (\theta - \theta_0),\qquad (17)$$

where ϵ and ζ are arbitrary constants, is a solution of equation (1), which will also satisfy (2) and (3), provided that ζ is infinitesimal, but related to ϵ by the condition

$$\epsilon + \zeta [\log r + 1]_{r=0} = 0.\qquad (18)$$
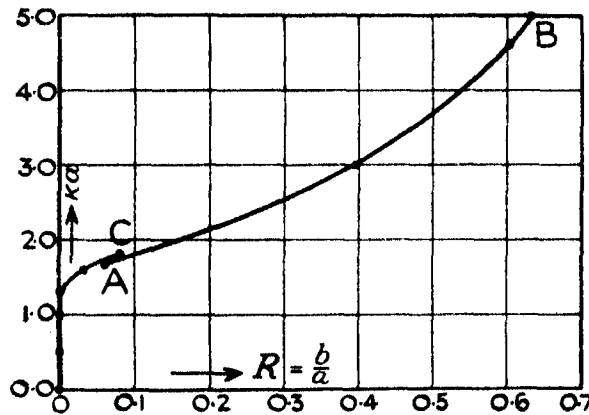
Fig. 1.

On the other hand, when the results (Table I) obtained for finite values of b/a are plotted, as in the curve AB of fig. 1, κa appears to be tending to a finite value as $b/a \to 0$. It thus appears that the frequency must rise very rapidly as the radius of the clamping circle increases from a zero value, and the conclusion may be confirmed by expanding the determinantal equation which is obtained by eliminating α, β, γ, δ from (11)—(14), on the assumption that κb is very small. When $s = 1$, the determinantal equation is easily thrown into the form*

$$A^4 \begin{vmatrix} AJ_1(A) - \eta J_2(A), & AY_1(A) - \eta Y_2(A), & AI_1(A) - \eta I_2(A), & AK_1(A) - \eta K_2(A), \\ J_2(A), & Y_2(A), & -I_2(A), & -K_2(A), \\ BJ_1(B), & BY_1(B), & -BI_1(B), & -BK_1(B), \\ J_0(B), & Y_0(B), & -I_0(B), & -K_0(B), \end{vmatrix}$$

$$= 0,\qquad (19)$$

* a being finite, it is legitimate to multiply the first two rows by this quantity. The complete equation contains an additional factor $1/b$, which has been cancelled out of equation (19), since it cannot be zero.

in which A and B are written for κa and κb respectively, and η is substituted (for brevity) in place of the quantity $(1-\sigma)$.   If we expand the determinant, substituting from (15) for the Bessel functions of argument B, the positive powers of B are found to be associated with powers of A not lower than the fourth, whilst the terms which are important when $B \to 0$ may be obtained from the determinantal equation

$$A^4 \begin{vmatrix} AJ_1(A)-\eta J_2(A), & AY_1(A)-\eta Y_2(A), & AI_1(A)-\eta I_2(A), & AK_1(A)-\eta K_2(A), \\ J_2(A), & Y_2(A), & -I_2(A), & -K_2(A), \\ 0, & -1, & 0, & 1, \\ 1, & \log B, & -1, & (\log B - E), \end{vmatrix}$$
$$= 0. \qquad (20)$$

Hence we find that the complete equation (19) may be written in the form

(positive powers of B) $\times$ (terms in A^4 and higher powers of A)

$$-[(3+\sigma) A^4 + (\text{higher powers of A})]$$

$$-(2 \log B - E)\left[\frac{A^8}{32}(3+\sigma) + (\text{higher powers of A})\right] = 0,$$

and when $A \to 0$ the significant terms in this equation are

$$-(3+\sigma) A^4 \left(1 + \frac{A^4}{16} \log B\right) = 0. \qquad (21)$$

The solution $A = 0$ (for all values of B) corresponds to the configuration of equilibrium, with which we are not at present concerned; the alternative solution may be written (since $A \log A \to 0$ with A) in the form

$$A^4 = -\frac{16}{\log R}, \text{ where } R = b/a. \qquad (22)$$

Hence, $A \to 0$ when $R \to 0$ (the result found previously), but

$$\frac{A}{R} = 2 \sqrt[4]{\left(\frac{-1}{R^4 \log R}\right)},$$

so that $\dfrac{A}{R}\left(\text{or } \dfrac{dA}{dR}\right) \to \infty$ as $R \to 0$.

The diagram shown in fig. 1 connects values of A (or κa) with values of R (or b/a); AB is a curve drawn through points which have been plotted from Table I, and OC is a curve obtained from the approximate determinantal equation (20), tables being employed to find the exact values of the Bessel functions in the first and second rows.   In this connection, it is convenient to employ the substitutions

$$AJ_2(A) = 2J_1(A) - AJ_0(A),$$
$$AY_2(A) = 2Y_1(A) - AY_0(A),$$
$$-AI_2(A) = 2I_1(A) - AI_0(A),$$
$$-AK_2(A) = 2K_1(A) - AK_0(A).$$

From the fact that the two curves very nearly overlap, it is evident that (20) approximates closely to the correct equation over the range considered ; a sufficiently exact transition from one curve to the other may be made by eye.

This completes the discussion of clamping for modes in which $s = 1$. When $s = 0$, the significant terms in (13) and (14) are

$$\alpha + \gamma + (\beta - \delta) \log \kappa b + \delta \mathrm{E} = 0$$

and

$$\frac{\beta - \delta}{\kappa b} = 0. \tag{23}$$

Both relations are satisfied if we write

$$\beta = \delta = -\frac{1}{\mathrm{E}} (\alpha + \gamma), \tag{24}$$

and (11) and (12) can then be expressed in terms of α and γ only. Eliminating α and γ, we obtain an equation in κa which may be solved, as before, by trial. The results depend to some extent upon the value of σ, which throughout this paper has been taken to be $0\cdot3$ (a representative value for steel) ; for this value, the first four calculated roots for κa are

$$\kappa a = 1\cdot937,\ 4\cdot573,\ 7\cdot79,\ 10\cdot94,$$

and the corresponding frequencies can be obtained from (6) in the form

$$p^2 = \frac{\mathrm{E}h^2}{\rho a^4} \times (5\cdot156,\ 160\cdot2,\ 1349,\ 5250), \tag{25}$$

where E is Young's Modulus for the material considered.

Fig. 2 illustrates the nature of the two gravest modes.
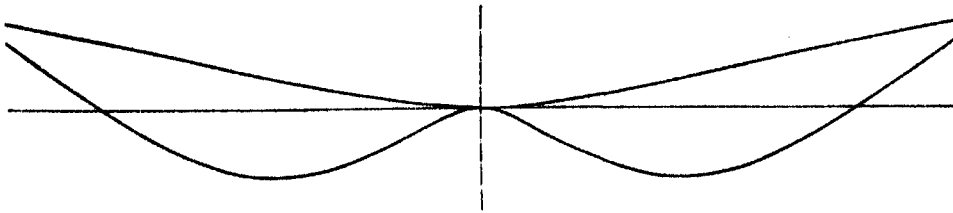
Fig. 2.

The variation of the frequency with the radius of the clamping circle, as found from the foregoing analysis, is exhibited in figs. 3–6, by means of curves which connect $p \sqrt{\left(\dfrac{\rho a^4}{\mathrm{E}h^2}\right)}$ (a non-dimensional quantity proportional to the frequency) with the ratio $R\,(= b/a)$; these show, as we should expect from physical considerations, that the effects of clamping are unimportant for small values of R, unless $s = 1$, when they increase very rapidly with the radius of the clamping circle.
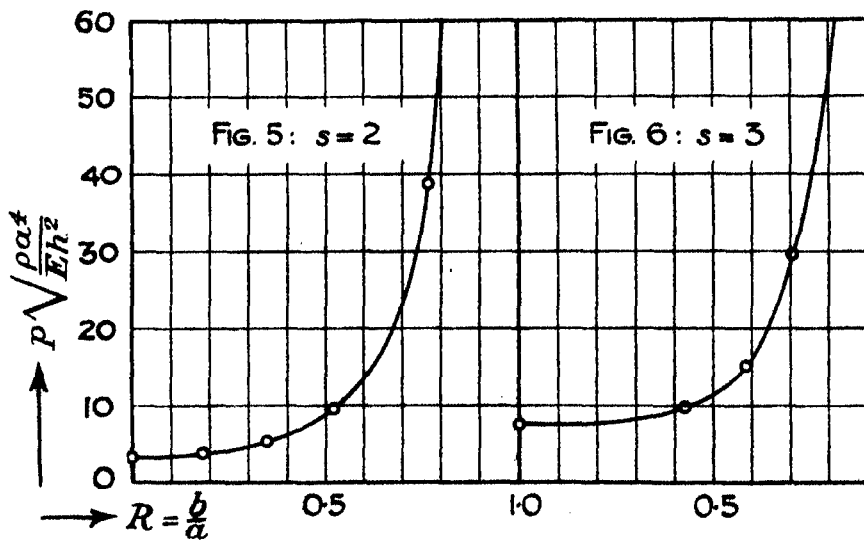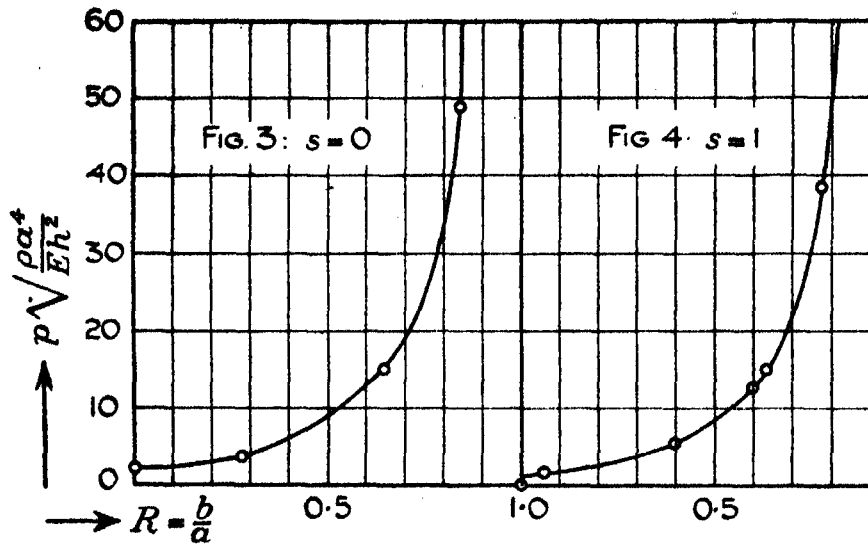
II. The Effects of Rotation.

(a) *Flexural Rigidity Neglected.*

§ 3. As in the paper on "Spinning Discs,"[*] we begin by considering the extreme case, in which the disc is so thin, and the rotation so rapid, that the

flexural forces are negligible. Under these conditions, the equation of transverse motion may be written in the form[*]

$$A(a^2-r^2)\left(\frac{\partial^2 w}{\partial r^2}+\frac{1}{r}\frac{\partial w}{\partial r}\right)-2Ar\frac{\partial w}{\partial r}+\left(\frac{p^2}{\omega^2}+s^2B-\frac{s^2Aa^2}{r^2}\right)w=0,\quad(5\text{A})$$

where
$$A=\frac{1}{8}(3+\sigma),\qquad B=\frac{1}{8}(1+3\sigma).\qquad(2\text{A})$$

If we write

$$\frac{p^2}{\omega^2}+s^2B=m(m+2)A,\qquad(8\text{A})$$

and
$$x=\frac{r^2}{a^2},$$

equation (5A) may be reduced to the form

$$4\frac{\partial}{\partial x}\left\{x(1-x)\frac{\partial w}{\partial x}\right\}+\left\{m(m+2)-\frac{s^2}{x}\right\}w=0.\qquad(26)$$

Again, if we write
$$w=yx^{s/2}$$

in (26), we obtain, as the differential equation to be satisfied by y,

$$4x(1-x)\frac{d^2y}{dx^2}+4\{1+s-(s+2)x\}\frac{dy}{dx}+\{m(m+2)-s(s+2)\}y=0,$$

and this may be written in the form

$$\frac{d^2y}{dx^2}+\frac{\gamma-(\alpha+\beta+1)x}{x(1-x)}\frac{dy}{dx}-\frac{\alpha\beta}{x(1-x)}y=0,\qquad(27)$$

where
$$\alpha=\tfrac{1}{2}(s-m),\qquad\beta=\tfrac{1}{2}(s+m+2),\qquad\gamma=s+1.\qquad(12\text{A})$$

Equation (27) is hypergeometric. The solution finite for $x=0$ is

$$\left.\begin{aligned}y_1&=C\left\{1+\frac{\alpha\beta}{1\cdot\gamma}x+\frac{\alpha(\alpha+1)\beta(\beta+1)}{1\cdot2\cdot\gamma(\gamma+1)}x^2+\ldots\right\},\\&\text{where C is an arbitrary constant,}\end{aligned}\right\}\qquad(28)$$

or
$$y_1=CF(\alpha,\beta,\gamma,x)$$

(in Gauss' notation). This is the solution which was discussed in the paper on "Spinning Discs," and the natural frequencies were obtained from the known theorem that, since

$$\gamma=\alpha+\beta,\qquad(13\text{A})$$

the expansion of $F(\alpha,\beta,\gamma,x)$ becomes logarithmically infinite at the edge $(x=1)$, unless it terminates.[†] Hence we must have

$$m=s+2n,\qquad(14\text{A})$$

where n is a positive integer.

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[*] The suffix previously attached to p is for the present omitted.
[†] Forsyth, 'Differential Equations,' § 113.

To take account of constraints which prevent transverse displacement along some circle (x = constant), we must consider the second solution of (27). When s is finite, this may be written in the form[*]

where
$$\begin{aligned}
y_2 &= C' x^{1-\gamma} F(\alpha', \beta', \gamma', x), \\
\alpha' &= \alpha + 1 - \gamma = -\tfrac{1}{2}(s+m), \\
\beta' &= \beta + 1 - \gamma = \tfrac{1}{2}(m+2-s), \\
\gamma' &= 2 - \gamma = 1 - s,
\end{aligned}\right\} \tag{29}$$

whilst if $s = 0$ (so that $\gamma = 1$) the second solution is[†]

$$y_2 = C' \left[F(\alpha, \beta, 1, x) \log x + \left\{ \frac{\alpha\beta}{1^2} \left(\frac{1}{\alpha} + \frac{1}{\beta} - \frac{2}{1} \right) x \right. \right.$$
$$\left. \left. + \frac{\alpha(\alpha+1)\beta(\beta+1)}{1^2 \cdot 2^2} \left(\frac{1}{\alpha} + \frac{1}{\alpha+1} + \frac{1}{\beta} + \frac{1}{\beta+1} - \frac{2}{1} - \frac{2}{2} \right) x^2 + \dots \right\} \right]. \tag{30}$$

C' denoting in each instance an arbitrary constant. Now, since

$$\gamma' = \alpha' + \beta',$$

the expansion of $F(\alpha', \beta', \gamma', x)$, in (29), is divergent unless it terminates. But it is easily seen, from (28), that if $F(\alpha, \beta, \gamma, x)$ terminates with the term in x^n, so that (14)A is satisfied, then $F(\alpha', \beta', \gamma', x)$ will terminate with the term in x^{s+n}, so that the solution given by (29) consists of a finite number of terms, beginning with a term in x^{-s} and ending with a term in x^n.

Again, it is evident that the quantity in twisted brackets on the right of (30) will terminate under the same conditions as $F(\alpha, \beta, \gamma, x)$, and at a term of the same order in x; moreover, the factor $F(\alpha, \beta, 1, x)$ in the first term is the solution found in (28). Hence, for all values of s, by suitably choosing the ratio of C' to C in the complete solution

$$y = y_1 + y_2,$$

we can make y (and hence w) vanish at any given radius; and *although the mode will be altered, the frequency of vibration will be unchanged.* When the constraint is applied at the centre, so that the radius at which w vanishes is indefinitely reduced, it is clear that the ratio of C' to C will be infinitesimal, so that the mode is unaffected by the constraint, except at the centre: at the centre it will be affected only if $s = 0$, since for other values of s the central displacement is zero in the first solution (28).

(b) *Flexural and Centrifugal Stresses both Operative.*

§ 4. When the centrifugal tensions and the flexural stiffness are both operative, the difficulties of an exact solution are much increased, since the

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[*] Forsyth, *op. cit.*, § 115.
[†] Forsyth, *op. cit.*, p. 251, Ex. 1.

modes as well as the frequencies of vibration depend upon the relative importance of the two systems. In regard to the gravest frequency corresponding to any given value of s, it was shown in the paper on "Spinning Discs"[*] that a *lower limit* to the frequency p can be obtained from the equation

$$p^2 = p_1^2 + p_2^2, \tag{34A}$$

where p_1 and p_2 are the values of p obtained by neglecting the flexural rigidity, and the effects of rotation, respectively.

The discussion just given shows that the values of p_1^2 are unaffected by clamping. Thus we may write, as in the earlier paper,

$$p_1^2 = \lambda \omega^2, \tag{20A}$$

where λ has values which may be found from the relations (2A), (8A) and (14A), given above. The following table (taken from the earlier paper, and amplified by the inclusion of a column for modes in which $s = 0$) gives numerical values for λ on the hypothesis that $\sigma = 0.3$, the value assumed previously :—

Table II.—Values of λ in the formula $p_1^2 = \lambda \omega^2$.

(N.B.—These values are not affected by clamping.)

	$s = 0.$	$s = 1.$	$s = 2.$	$s = 3.$
$n = 0$	0	1	2·35	4·05
$n = 1$	3·3	5·95	8·95	12·3
$n = 2$	9·9	14·2	18·85	23·85
$n = 3$	19·8	25·75	32·05	38·7

The results of Section I show that the radius of clamping has an influence upon the value of p_2^2, but that when this radius is indefinitely reduced the only frequencies affected by clamping are those corresponding to the modes in which $s = 0$. Hence, writing

$$p_2^2 = \mu \frac{Eh^2}{\rho a^4}, \tag{21A}$$

as in the "Spinning Discs" paper, we have the following table of values for μ, of which only the second column ($s = 0$, centre clamped) is new : σ is again assumed to have the value 0·3.

[*] *Loc. cit.*, § 4.

Table III.—Values of μ in the formula $p_s{}^2 = \mu \dfrac{Eh^2}{\rho a^4}$.

(N.B.—Clamping is confined to the centre of the Disc.)

	$s = 0.$		$s = 1.$	$s = 2.$	$s = 3.$
	Centre free.	Centre clamped.	(These values are not affected by central clamping.)		
$n = 0$	0	5·16	0*	10·61	56·87
$n = 1$	29·67	160·2	154·3	443·9	1040
$n = 2$	577	1349	1222	2624	4285
$n = 3$	2983	5250	5266	8574	13287

* But *cf.* the discussion of this case given in §2.   When the radius of clamping is finite, though very small, 1·05 may be taken as a representative value of μ.

By means of these tables (or of Table II and figs. 3—6, when the radius of clamping is finite) the lower limit given by (34A) can be quickly calculated. But it is evident that no allowance will be made in this way for the effect of rotation in regard to the modes in which $s = 0$: these, in a disc of which the centre is clamped, must be conditioned in the main by the flexural system, and will necessarily be such as will bring the centrifugal system into operation.

§ 5. In the "Spinning Discs" paper,* closely approximate results were obtained by means of Rayleigh's method of an assumed type,† in which the potential and kinetic energies are calculated on the basis of an assumed expression for w, and the frequencies determined from the condition that their sum remains constant in the vibration.   A frequency thus calculated is stationary for slight variations of the type, and a good approximation can, therefore, be obtained in this way if the type be suitably chosen.   Moreover, in the case of the gravest mode of all, it is known that the frequency will be overestimated, and in the present problem this statement applies also to the gravest mode corresponding to any definite value of s.   Prof. Lamb has made use of this fact in devising a method whereby the accuracy of Rayleigh's method may be improved; it consists in the inclusion of a variable parameter in the assumed expression for w, the value of this parameter being afterwards adjusted so as to make the calculated frequency a minimum.‡   Using this

* *Loc. cit.*, p. 276.
† 'Theory of Sound,' vol. 1, §§ 88, 89.
‡ *Cf.* his paper " On the Vibrations of an Elastic Plate in Contact with Water," ' Roy. Soc. Proc.,' A, vol. 98, pp. 205-216 (1920), which appears to be the earliest illustration of the method.

device, the gravest frequency of vibration in a mode having two nodal diameters was estimated, for a non-rotating disc, with an error less than ½ per cent.[*]

Applying these methods to the determination of the gravest frequency in modes for which $s = 0$, we have as expressions for the potential and kinetic energies, in polar co-ordinates[†] :—

V_1 = Potential Energy of the Centrifugal Forces,

$$= 2\pi h \int_0^a P \left(\frac{\partial w}{\partial r}\right)^2 r\,dr, \tag{31}$$

where $\qquad P = A(a^2 - r^2)\rho\omega^2,$ $\hfill$ (1A)

and A is given by equation (2A) above ;

V_2 = Potential Energy of Flexure,

$$= \frac{2\pi E h^3}{3(1-\sigma^2)} \int_0^a \left\{ \left[\frac{\partial^2 w}{\partial r^2} + \frac{1}{r}\frac{\partial w}{\partial r}\right]^2 - \frac{2(1-\sigma)}{r}\frac{\partial w}{\partial r}\cdot\frac{\partial^2 w}{\partial r^2}\right\} r\,dr ; \tag{32}$$

T = Kinetic Energy of the Motion,

$$= 2\pi\rho h \int_0^a \left(\frac{\partial w}{\partial t}\right)^2 r\,dr. \tag{33}$$

In the application of Rayleigh's method, an assumed form for w is substituted in these expressions, and we obtain an estimate of the frequency from the energy equation

$$V_1 + V_2 + T = \text{constant.} \tag{34}$$

We begin with the extreme case in which ω is zero, since accurate results are here available for comparison. The simplest expression for w which satisfies the conditions that w and $\partial w/\partial r$ vanish at the centre is

$$w = k\frac{r^2}{a^2}\sin p_2 t, \tag{35}$$

where k is an arbitrary constant. Substituting this expression in (32) and (33), we have

$$V_2 = \frac{8\pi k^2 E h^3}{3(1-\sigma)a^2}\sin^2 p_2 t, \left.\rule{0pt}{20pt}\right\}$$
$$T = \frac{\pi}{3}k^2 p_2^2 \rho h a^2 \cos^2 p_2 t, \left.\rule{0pt}{20pt}\right\}$$

and from (34) we obtain the value

$$p_2^2 = \frac{8}{1-\sigma}\cdot\frac{E h^2}{\rho a^4},$$

whence $\qquad \mu = 11\cdot429,$ when $\sigma = 0\cdot3.$ $\hfill$ (36)

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[*] *Vide* § 5 of the "Spinning Discs" paper, equation (52).
[†] *Cf.* equations (25)–(29) of the "Spinning Discs" paper.

Comparing this result with the correct figure (5·16) given in Table III, we see that it is over 100 per cent. in error. To obtain a closer approximation, we may employ the artifice of Prof. Lamb, and assume, in place of (35), that

$$w = \alpha \frac{r^2}{a^2}\left(1 + \beta \frac{r^2}{a^2}\right) \sin p_2 t, \tag{37}$$

α and β being arbitrary constants. Then we have

$$V_2 = \frac{8\pi \alpha^2 E h^3}{3(1-\sigma^2)a^2}\left\{(1+\sigma)(1+4\beta) + \frac{4}{3}(5+3\sigma)\beta^2\right\} \sin^2 p_2 t,$$

$$T = \pi a^2 p_2^2 \rho h a^2 \left\{\frac{1}{3} + \frac{\beta}{2} + \frac{\beta^2}{5}\right\} \cos^2 p_2 t,$$

and (34) gives the expression

$$p_2^2 = \frac{8}{3(1-\sigma^2)} \frac{E h^2}{\rho a^4}\left\{\frac{(1+\sigma)(1+4\beta) + 4/3(5+3\sigma)\beta^2}{1/3 + \beta/2 + \beta^2/5}\right\}. \tag{38}$$

Thus we have, in equation (21A) above, the expression

$$\mu = \frac{L + 2M\beta + N\beta^2}{l + 2m\beta + n\beta^2}, \tag{39}$$

where, if $\sigma = 0·3$,

$$L = \frac{8}{3(1-\sigma)} = 3·81, \qquad l = \frac{1}{3},$$

$$M = \frac{16}{3(1-\sigma)} = 7·62, \qquad m = \frac{1}{4}, \tag{40}$$

$$N = \frac{32(5+3\sigma)}{9(1-\sigma^2)} = 23·06, \qquad n = \frac{1}{5}.$$

The stationary values of μ are given by the quadratic

$$(ln - m^2)\mu^2 - (lN + nL - 2mM)\mu + (LN - M^2) = 0,$$

or

$$\frac{1}{240}\mu^2 - 4·64\mu + 29·79 = 0,$$

whence the gravest value of p_2^2, in (38), is given by

$$p_2^2 = 6·457 \frac{E h^3}{\rho a^4}, \text{ approximately}, \tag{41}$$

a result which is still 25 per cent. in error.

It is evident that the additional boundary conditions at the centre of the disc increase the difficulty of finding a suitable assumed form for w. The value of β which corresponds to (41) is $-0·275$ approximately, and when this is substituted in (37) the resulting form for w is found to differ materially from the correct form shown in fig. 2. After several failures to guess a better form, the plan was adopted of calculating the deflection of the disc when clamped at its centre and subjected to a loading varying in intensity as

some power of the radial distance, the edge being assumed to be free from shearing forces, but not necessarily from stress-couples. This deflection, multiplied by $\sin p_2 t$, was taken as the assumed form of w, and the frequency was then calculated by Rayleigh's method: finally, the index of r in the assumed intensity of loading was chosen so as to make the calculated frequency a minimum. In this way, the advantages of Prof. Lamb's device are retained, whilst the assumed mode, independently of the value given to the variable parameter, satisfies three out of the four boundary conditions.

It is easily verified that the expression

$$\mathrm{W} = \mathrm{C} \left\{ r^q - \frac{q^2(q-2)}{4} a^{q-2} r^2 \log \frac{r}{a} \right\}, \tag{42}$$

where C is an arbitrary constant, gives the displacement corresponding to a loading of intensity

$$Z = \mathrm{D} \left[\frac{1}{r} \frac{d}{dr} r \frac{d}{dr} \right]^2 \mathrm{W} = \mathrm{CD} q^2 (q-2)^2 r^{q-4}, \tag{43}$$

where $\mathrm{D} = \frac{2}{3} \frac{\mathrm{E}h^3}{1-\sigma^2}$; it may also be shown to satisfy the second of the edge conditions (2), together with both of the clamping conditions (3), provided that $q > 1$ and $q \neq 2$.

For a value of q close to 3 it will also satisfy the first of (2); but it is preferable to leave q indeterminate for the present, and to choose it subsequently so as to make the calculated frequency a minimum. We find that

$$\int_0^a r \left[\frac{d^2\mathrm{W}}{dr^2} + \frac{1}{r} \frac{d\mathrm{W}}{dr} \right]^2 dr = \mathrm{C}^2 q^4 a^{2(q-1)} \left[\frac{1}{2(q-1)} - \frac{2(q-1)(q-2)}{q^2} + \frac{(q-2)^2}{4} \right],$$

and

$$\int_0^a \frac{d\mathrm{W}}{dr} \cdot \frac{d^2\mathrm{W}}{dr^2} dr = \mathrm{C}^2 q^2 a^{2(q-1)} \left[\frac{1}{2} - \frac{q(q-2)}{4} + \frac{q^2(q-2)^2}{32} \right],$$

whence the potential energy of flexure in the mode

$$w = \mathrm{W} \sin pt \tag{44}$$

is

$$\mathrm{V}_2 = \frac{2\pi \mathrm{E}h^3}{3(1-\sigma^2)} \mathrm{C}^2 q^2 a^{2(q-1)} \sin^2 pt \left[\frac{q^2}{2(q-1)} - 2(q-1)(q-2) + \frac{q^2(q-2)^2}{4} \right.$$
$$\left. -(1-\sigma) \left\{ 1 - \frac{q(q-2)}{2} + \frac{q^2(q-2)^2}{16} \right\} \right]. \tag{45}$$

The kinetic energy of the motion is

$$\mathrm{T} = 2\pi \rho h p^2 \cos^2 pt \int_0^a r \mathrm{W}^2 dr,$$
$$= 2\pi \rho h p^2 \mathrm{C}^2 a^{2(q+1)} \cos^2 pt \left[\frac{1}{2(q+1)} + \frac{q^2(q-2)}{2(q+4)^2} + \frac{q^4(q-2)^2}{16 \cdot 108} \right] \tag{46}$$

The expression for the frequency is therefore given by equation (21A) above, if

$$\mu = \frac{q^2}{3(1-\sigma^2)} \times$$

$$\left[\frac{\frac{q^2}{2(q-1)} - 2(q-1)(q-2) + \frac{q^2(q-2)^2}{4} - (1-\sigma)\left\{ 1 - \frac{q(q-2)}{2} + \frac{q^2(q-2)^2}{16} \right\}}{\frac{1}{2(q+1)} + \frac{q^2(q-2)}{2(q+4)^2} + \frac{q^4(q-2)^2}{16 \cdot 108}} \right].$$

$$(47)$$
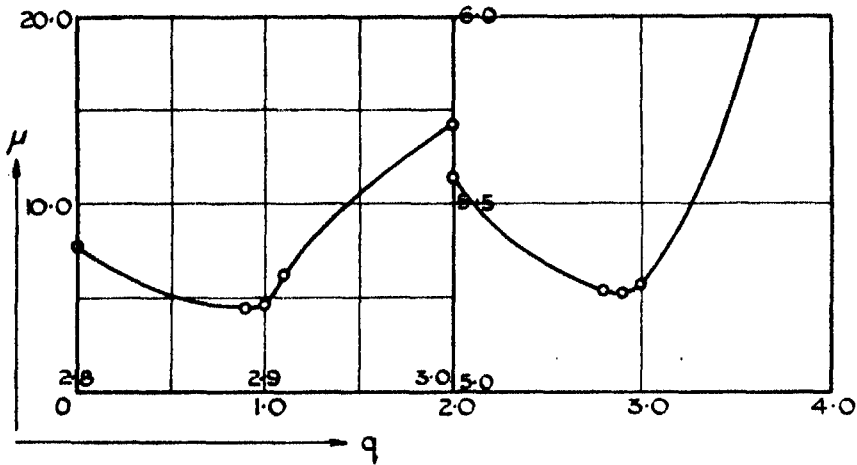
Fig. 7.

We have seen that the conditions to be satisfied at the centre require that q shall be greater than 1 and not equal to 2. Subject to this restriction, we may choose q so as to make μ, in (47), a minimum; the required value is best determined by plotting μ against q, as shown in fig. 7, where the important part of the curve is also plotted on a much enlarged scale. Taking σ as equal to 0·3, it is found that the expression μ has a minimum value of 5·22 when $q = 2·89$. This is an error of less than 1·2 per cent. in the value of μ, or less than 0·6 per cent. on the frequency, which is a very satisfactory result: but the rapid rise of μ, as q departs from the optimum value, serves to explain why such serious overestimates were obtained from what might have been considered reasonable assumptions for the form of w.

We proceed to consider the effects of rotation. Substituting for w, in (31), from (42) and (44), we have

$$V_1 = 2\pi\rho\omega^2 Ah \, C^2 q^2 a^{2q+2} \sin^2 pt \left[\frac{1}{2q} - \frac{q^2(q-2)}{2(q+2)^2} + \frac{q^2(q-2)^2}{8 \cdot 16} \right.$$

$$\left. - \left\{ \frac{1}{2(q+1)} - \frac{q(q+2)(q-2)}{2(q+4)^2} + \frac{5 q^2(q-2)^2}{3 \cdot 18 \cdot 16} \right\} \right].$$

The kinetic energy is given by (46), as before. Hence, by (34), the expression for the frequency will be of the form (20A), where

$$\lambda = Aq^2 \left[\frac{\dfrac{1}{2q(q+1)} - \dfrac{q(q-2)(q^2+2q-4)}{(q+2)^2(q+4)^2} + \dfrac{7q^2(q-2)^2}{16 \cdot 27 \cdot 8}}{\dfrac{1}{2(q+1)} + \dfrac{q^2(q-2)}{2(q+4)^2} + \dfrac{q^4(q-2)^2}{16 \cdot 108}} \right]. \qquad (48)$$

λ, as determined from this expression, may be plotted against q, in the manner of fig. 7. Its minimum value is 0·416, and occurs when $q = 3·295$: like that of μ, it is sharply defined, and the optimum value for q will clearly depend in the general case upon the relative importance of the flexural and centrifugal terms. But if we regard it as determined entirely by the flexural system, the value of λ will be only slightly, if at all, in excess of 0·5; adopting this value as sufficiently accurate for practical purposes, we may calculate the gravest frequency in a symmetrical mode from the formula

$$p^2 = \lambda\omega^2 + \mu \frac{Eh^2}{\rho a^4},$$

where

$$0 < \lambda < 0·5,$$

and

$$5·16 < \mu < 5·22. \qquad (49)$$

A closer approximation could, of course, be obtained, in any particular instance, by using the curves for λ and μ. Alternatively, by assuming the *mode* to be unchanged by rotation (so that μ is given by Table III), and employing (31), (33) and (34) for the calculation of λ, we could obtain upper limits to the value of this quantity, for use in the general formula (49): Table II, as we have seen, gives lower limits. The calculations would need to be done graphically.

Dispersion Formulæ and the Polarisation of Scattered Light: with Application to Hydrogen.

By T. H. HAVELOCK, F.R.S.

Introduction and Summary.

Since Lord Rayleigh's experimental study of the polarisation of light scattered by gases, the subject has been examined theoretically from various points of view; in particular by the late Lord Rayleigh,[*] M. Born,[†] Sir J. J. Thomson,[‡] and R. Gans.[§] The object of the following paper is to connect the polarisation of light scattered by a simple homogeneous medium with the constants of the dispersion formula for that medium. The result of the calculation gives the ratio of the intensities of the two polarised components for all wave-lengths for which the dispersion formula is valid. Although the expressions can be generalised, they are given in the first instance in their simplest form.

Assuming the medium to be a gas whose approximate dispersion formula contains only one natural frequency in the ultra-violet, this is generalised by supposing the molecules to be anisotropic; the single natural frequency is then replaced by a triplet, or by a doublet for molecules with axial symmetry. In the latter case the dispersion formula is, in the usual notation

$$n^2 - 1 = \tfrac{1}{3} C \left\{ (p_1^2 - p^2)^{-1} + 2 (p_2^2 - p^2)^{-1} \right\}.$$

The three constants of the formula are left to be determined from experimental results. For this purpose it is necessary to have accurate values of the refractive index over a large range of wave-lengths, and hydrogen has been chosen as the most suitable. Two formulæ of this type are obtained, one of prolate form and the other oblate; both express the dispersion with sufficient accuracy over the range 5462 to 1854 Ångström units. Incidentally a comparison is made with previous formulæ such as those of Cuthbertson, Lundblad, Debye and Sommerfeld.

The expressions for the ratio of the intensities of the two polarised components of the scattered light are based directly upon Rayleigh's calculations; an obvious interpretation of the coefficients brings them into relation

* Rayleigh, 'Phil. Mag.,' vol. 35, p. 373 (1918); or 'Scientific Papers,' vol. 6, p. 540.
† M. Born, ' Deutsch. Phys. Gesell.,' vol. 19, p. 243 (1917), and vol. 20, p. 16 (1918).
‡ Sir J. J. Thomson, ' Phil. Mag.,' vol. 40, p. 393 and p. 713 (1920).
§ R. Gans, ' Ann. der Phys.,' vol. 65, p. 97 (1921).

with the particular type of dispersion formula. In the special case given above, if the formula is written as

$$n^2 - 1 = \tfrac{1}{8}\{n_1{}^2 - 1 + 2(n_2{}^2 - 1)\},$$

the corresponding ratio of intensities when the primary beam is unpolarised is

$$6(n_1{}^2 - n_2{}^2)^2 / \{45(n^2 - 1)^2 + 7(n_1{}^2 - n_2{}^2)^2\}.$$

The values have been calculated, at various wave-lengths, for hydrogen from the two dispersion formulæ; the numerical results are in substantial agreement with the revised experimental value 0·0383 obtained by Lord Rayleigh. Other dispersion formulæ are also examined from this point of view. It is shown that their failure to give the correct dispersion in the extreme ultra-violet is accompanied by a corresponding divergence in the ratio of the intensities of the components of scattered light.

It is hoped to extend the investigation to a comparative study of gases or other media for which the available experimental results are suitable for analysis by this method.

Dispersion with Anisotropic Molecules.

In deriving the simplest type of dispersion formula,

$$n^2 - 1 = C/(p_0{}^2 - p^2), \tag{1}$$

it is assumed that the molecules are isotropic, the electric polarisation being always in the direction of the electric force. The formula (1) has been generalised in various ways; for instance, by direct summation of terms on the right for different natural frequencies, or by more precise specification of the local electric field leading to similar formulæ with $(n^2 - 1)/(n^2 + 2)$ or more general forms on the left, or again by using some definite theory of atomic or molecular structure. We shall leave these out of account and consider a simple gaseous medium composed of anisotropic molecules with random distribution and orientation. Assume that each molecule has three principal axes of polarisation fixed relative to the molecule and that the connection between the polarisation (P_1, P_2, P_3) and the electric field (F_1, F_2, F_3) is given by three equations of the form

$$\frac{\partial^2 P_1}{\partial t^2} + p_1{}^2 P_1 = kF. \tag{2}$$

It should be noted that for simplicity we assume the coefficient k to be the same for the three components. Let $O(x, y, z)$ be axes fixed in space, and consider a plane wave travelling in the direction Ox with the electric force Z parallel to Oz and proportional to e^{ipt}. The directions of the principal axes of any molecule may be specified by two angular co-ordinates θ, ϕ; and we

obtain F_1, F_2 and F_3 by resolving Z along the principal axes. Further, the mean polarisation is obtained by summation for all possible orientations of the molecules, assuming random distribution with respect to θ and ϕ. Finally, if P is the component of mean polarisation parallel to Oz, the dispersion formula is derived from the relation $P/Z = (n^2-1)/4\pi$. The process gives readily the formula

$$n^2-1 = \tfrac{1}{3} C \left(\frac{1}{p_1^2-p^2} + \frac{1}{p_2^2-p^2} + \frac{1}{p_3^2-p^2} \right), \tag{3}$$

where C has been written for $4\pi Nk$, with N as the number of molecules per unit volume.

In Drude's interpretation of (1) in terms of vibrating electrons, the value of C is $4\pi Ne^2/m$ or some integral multiple thereof; and the same holds for the formula (3). It is well known that the value of e/m derived from dispersion formulæ is less than the accepted value for an electron. This may be ascribed, no doubt, to unknown coupling effects between vibrating electrons, and it might be supposed that the generalisation from (1) to (3) might remove this discrepancy in part; however, we shall find it better not to make any assumption in this respect, but to leave C to be determined from the experimental values of the dispersion.

It is convenient to write (3) in the form

$$n^2-1 = \tfrac{1}{3}(n_1^2-1+n_2^2-1+n_3^2-1), \tag{4}$$

where $n_1^2-1 = C/(p_1^2-p^2)$; etc.

The quantities n_1, n_2, n_3 are subsidiary principal indices; in fact, if the molecules were all orientated in the same way, without thereby introducing any effects due to mutual interference, the medium would be optically a crystal with these principal indices.

If the molecules have an axis of symmetry, so that $p_2 = p_3$, the formulæ become

$$n^2-1 = \tfrac{1}{3} C \left(\frac{1}{p_1^2-p^2} + \frac{2}{p_2^2-p^2} \right), \tag{5}$$

$$= \tfrac{1}{3} \{ (n_1^2-1) + 2(n_2^2-1) \}. \tag{6}$$

The formula (5) is to be calculated from experimental results as a three-constant formula. If it does not prove adequate it may be necessary to use (3) or its more general forms, or, further, to introduce into (3) and (5) some of the extensions which were mentioned in connection with formula (1).

It may be noted that, instead of, as in (1), a single resonance period at which n becomes infinite, we have in (3) a triplet and in (5) a doublet; but the positions of maximum absorption or reflection cannot be discussed satisfactorily without introducing terms of some kind to represent dissipation.

Scattering by Anisotropic Molecules.

There are several factors in Rayleigh's well-known expression for the intensity of light scattered by a medium composed of a random distribution of small particles or molecules, each with spherical symmetry. Each particle behaves like a vibrating doublet, and hence there is a factor λ^{-4}, where λ is the wave-length; the factor with which we are concerned here is that which expresses the optical properties of the particles, namely $(n^2 - 1)^2$, where n is the refractive index of the medium.

In the paper referred to above,[*] an extension was made to scattering by a cloud of similar small particles of any shape and oriented at random. We quote Rayleigh's results for the ratio of intensities of the two polarised components in the light scattered at right angles, the principal component being that which vibrates parallel to the primary vibrations, and the subordinate component (vanishing for spherical particles) being that in which the vibrations are perpendicular to the primary vibrations. The scattering effect of a particle, or molecule, is represented by coefficients; taking first the case of particles with an axis of symmetry, these coefficients are written A, A, C. Then by a simple, but general, argument, expressions are found for the aggregate intensities due to a large number of particles with their positions and their axes distributed at random. The results are: (i) if the primary light is plane polarised, the ratio of the intensities of the two components is

$$(C-A)^2/(8A^2 + 3C^2 + 4AC),\tag{7}$$

and (ii) if the primary light is unpolarised, the ratio is

$$2(C-A)^2/(9A^2 + 4C^2 + 2AC).\tag{8}$$

For the more general case, when each particle has three principal axes, the coefficients being A, B, C, the corresponding results are in case (i)

$$\frac{A^2 + B^2 + C^2 - BC - CA - AB}{3(A^2 + B^2 + C^2) + 2(BC + CA + AB)},\tag{9}$$

and in case (ii)

$$\frac{2(A^2 + B^2 + C^2 - BC - CA - AB)}{4(A^2 + B^2 + C^2) + BC + CA + AB}.\tag{10}$$

The paper concludes with the remark that "the problem of an ellipsoidal particle of uniform dielectric quality can be no more than illustrative of what happens in the case of a molecule; but we may anticipate that the general form, with suitable values of A, B, C, still applies, except it may be under special circumstances, where resonance occurs, and where the effective values of the coefficients may vary greatly with the wave-length of the light."

[*] Rayleigh, 'Scientific Papers,' vol. 6, p. 540.

The interpretation of the coefficients which we make now is obvious when we remember their values for spherical particles when $A = B = C$, and we take into account the corresponding dispersion formulæ (4), (5) and (6); in the notation introduced there, we take

$$A : B : C = n_1^2 - 1 : n_2^2 - 1 : n_3^2 - 1. \tag{11}$$

Substituting these values in (7), (8), (9), (10) we obtain the required forms. It is convenient, instead of leaving them entirely in terms of the sub-indices n_1, n_2, n_3, to introduce the total refractive index n, in accordance with (4) and (6). Writing the results in the same order as in (7)–(10), the ratios in the four cases are

$$\frac{3\,(n_1^2 - n_2^2)^2}{45\,(n^2 - 1)^2 + 4\,(n_1^2 - n_2^2)^2}, \tag{12}$$

$$\frac{6\,(n_1^2 - n_2^2)^2}{45\,(n^2 - 1)^2 + 7\,(n_1^2 - n_2^2)^2}, \tag{13}$$

$$\frac{3\,\{(n_2^2 - n_3^2)^2 + (n_3^2 - n_1^2)^2 + (n_1^2 - n_2^2)^2\}}{90\,(n^2 - 1)^2 + 4\,\{(n_2^2 - n_3^2)^2 + (n_3^2 - n_1^2)^2 + (n_1^2 - n_2^2)^2\}}, \tag{14}$$

$$\frac{6\,\{(n_2^2 - n_3^2)^2 + (n_3^2 - n_1^2)^2 + (n_1^2 - n_2^2)^2\}}{90\,(n^2 - 1)^2 + 7\,\{(n_2^2 - n_3^2)^2 + (n_3^2 - n_1^2)^2 + (n_1^2 - n_2^2)^2\}}. \tag{15}$$

The first term in the denominator in each case is the same as if the molecules were isotropic; it may be said to represent the effect of random distribution as regards position. The anisotropy of the molecules, and the random distribution of their axes as regards orientation, contribute to the intensities of both polarised components, and are represented by the numerator and the second term in the denominator in each case.

These expressions are obviously associated with dispersion formulæ of types (4) and (5) with $n^2 - 1$ expressed as a function of the wave-length and proportional to density; it may be anticipated that they will have a similar range of application. They are capable of generalisation in a similar manner to the dispersion formulæ. They could also be extended in accordance with other methods of obtaining the intensity of scattered light, for instance, Einstein's more general method for isotropic molecules, based on a statistical view of the fluctuations of density. The latter idea has been applied to a gas with anisotropic molecules by Born in the paper already quoted. Born distinguishes between scattering due to fluctuations of density and that due to variations in orientation; adding the two, his results for the total scattering are given in general form in terms of functions of the wave-length.

The special case (13) which we shall use—which we have derived directly from Rayleigh's expressions—can, in fact, be deduced from Born's formulæ when they are interpreted from the present point of view.

Dispersion Formulæ for Hydrogen.

The most recent determinations of the dispersion of hydrogen are those of M. Kirn,* over wave-lengths ranging from 5462 to 1854 Ångström units. His values agree well with those of Koch, whose shortest wave-length was 2302, and with those of Cuthbertson in the visible spectrum. We shall use Kirn's results, and the wave-lengths and values of $(n-1).10^7$ are given in the first and second columns of Table I.

We try now to fit these with a formula

$$n^2-1 = C\left(\frac{1}{\lambda_1{}^{-2}-\lambda^{-2}} + \frac{2}{\lambda_2{}^{-2}-\lambda^{-2}}\right). \tag{16}$$

Most dispersion formulæ derived from experimental results are expressed in Cauchy's form, a power series in λ^2; in that case the formula can be made to have any required degree of accuracy, or, with a limited number of terms of the series, the coefficients for the best possible agreement can be found by the method of least squares. Such methods, adapted to the form (16), would become very laborious. It was decided not to attempt adjusting the constants, but simply to determine them from three pairs of values of n and λ; the values of λ chosen were the two extremes 5462 and 1854, together with 2753.

We have then three equations of the type

$$\alpha' = C\left(\frac{1}{x_1-x'} + \frac{2}{x_2-x'}\right), \tag{17}$$

from which to determine C, x_1, and x_2. By elimination an equation of the fifth degree in x_1 is obtained, and a similar equation for x_2. The numerical coefficients were calculated so as to allow the roots of these equations to be found to four significant figures. Taking a pair of values so found, successive approximation was made until the three values of C from equations (17) were the same to a sufficient degree of accuracy. In this way we obtain the formula, with λ in centimetres,

$$n^2-1 = 1\cdot2429583 \times 10^{-4}\left\{\frac{1}{1\cdot032551-10^{-10}\lambda^{-2}} + \frac{2}{1\cdot638331-10^{-10}\lambda^{-2}}\right\}. \tag{18}$$

The values of n were then calculated from (18) over the whole range, and the differences between the calculated and observed values of $(n-1).10^7$ are shown in Column 3 of Table I. The differences are within the possible experimental errors, and the agreement is sufficiently good; especially taking into account that equal weight has been given to the value in the extreme ultra-violet where the possible experimental error is greatest, and that the

* M. Kirn, 'Ann. der Phys.,' vol. 64, p. 566 (1921).

constants have not been adjusted to give the best average agreement. Returning to the equations in x_1 and x_2 derived from (17) there are other possible roots. We find the equation in x_2 has a root near 1·169 ; further, it is seen that in order to make a possible pair there should be a root in x_1 about the value 2. In this case the equation in x_1 has no actual root, but it was found by graphical methods that a slight alteration in the values of α in (17) would have given such a root ; and, further, that the corresponding value of C would have been practically the same as in (18). We therefore assume the same value of C, and determine x_1 and x_2 from the two equations of (17) corresponding to the two wave-lengths 5462 and 1854 ; it will be seen that this also very nearly agrees with the equation for the intermediate wavelength 2753. We have now a second dispersion formula

$$n^2-1 = 1\cdot2429583 \times 10^{-4} \left\{ \frac{1}{2\cdot088392-10^{-10}\lambda^{-2}} + \frac{2}{1\cdot169513-10^{-10}\lambda^{-2}} \right\},$$

$$(19)$$

The differences between the values of $(n-1).10^7$ calculated from (19) and the observed values are shown in Column 4 of Table I. It will be seen that there is the same degree of accuracy as with formula (18).

It is perhaps unnecessary to remark that in numerical calculation of formulæ of this type with three constants at our disposal, a certain amount of variation of the values of the constants is possible, without making any great difference to the agreement between observed and calculated values of the dispersion. It has therefore been thought desirable to state explicitly the process adopted in obtaining (18) and (19). This point may be illustrated by an empirical formula given by Kirn to express his experimental results, without stating how the constants were determined, namely,

$$(n-1) \cdot 10^8 = \frac{1220070}{118\cdot6371-10^{-8}\lambda^{-2}} + \frac{581198\cdot1}{175\cdot3273-10^{-8}\lambda^{-2}}. \qquad (20)$$

The differences between observed values and those calculated from (20) are shown in Column 5 of Table I. It is of interest to notice that this empirical formula is nearly of the type we require, with one numerator twice the other.

Returning to (18) and (19) we have two dispersion formulæ for hydrogen, one being of the prolate and the other of the oblate type. This, of course, has no reference to actual shape of molecules ; it is using the words in the sense in which they are used in describing uniaxial crystals, such as hydrogen might be on this view, with the molecules all oriented the same way. It cannot be said that the available data enable us to decide between the alternatives. If the constant C in (18) and (19) agreed with Drude's inter-

Table I.—Differences between Calculated and Observed Values of
$(n-1) \cdot 10^7$ for Hydrogen.

λ.	$(n-1) \cdot 10^7$ (obs.).	(18).	(19).	Kirn.	Cuthbert-son.	Lundblad.	Debye.
5462·260	1395·50	0·00	0·00	−0·26	+ 0·90	+0·07	−26·0
4359·567	1417·73	+0·22	+0·31	−0·07			
4078·991	1426·32	+0·23	+0·37	−0·01			
4047·698	1427·41	+0·21	+0·35	+0·01			
3342·438	1461·33	+0·10	+0·36	+0·25	− 3·24	−0·16	−28·0
2968·141	1491·01	+0·25	+0·60	+0·40			
2894·452	1498·59	+0·15	+0·51	+0·42	—	—	−36·0
2753·615	1515·00	0·00	+0·41	+0·48	− 7·37	−0·15	
2535·560	1546·90	−0·12	+0·35	+0·57			
2379·115	1576·81	−0·43	+0·07	+0·61			
2302·870	1594·18	−0·58	−0·08	+0·60	—	+0·49	
1990·469	1693·95	−0·64	−0·46	+0·25			
1935·846	1718·24	−0·46	−0·22	+0·07	−27·63	+5·41	
1862·749	1755·41	−0·01	+0·01	−0·20			
1854·637	1759·96	0·00	0·00	+0·78	−32·25	+8·34	−58·0

pretation, its value, for two electrons per molecule, would be 1·6059; the smaller value 1·24296 is required for a simple equivalent molecule, with anisotropic properties of polarisation, without specifying details of structure.

Calculating the value of n^2 when $\lambda = \infty$, we obtain 1·000272 from both (18) and (19). This is the value of the dielectric constant given by Tangl,[*] who also remarks that it agrees with the value of n^2_∞ derived from dispersion formulæ of Cauchy's type. This may be taken to confirm the view that the hydrogen molecule contains no permanent doublets, such as have been invoked to explain the variation of dielectric constants with temperature in certain cases.[†]

Finally, for the wave-lengths at which n becomes infinite, we have from (18) the doublet

$$\lambda_1 = 984·07 ; \qquad \lambda_2 = 781·3 ; \tag{21}$$

and from (19) the doublet

$$\lambda_1 = 699·2 ; \qquad \lambda_2 = 924·7. \tag{22}$$

It is of interest to compare these formulæ with others which have been given for hydrogen.

The simple formula due to Cuthbertson[‡] was based on observations over a

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[*] K. Tangl, 'Ann. der Phys.,' vol. 26, p. 59 (1908).
[†] H. Riegger, 'Ann. der Phys.,' vol. 59, p. 753 (1919).
[‡] C. and M. Cuthbertson, 'Roy. Soc. Proc.,' A, vol. 83, p. 165 (1910).

comparatively short range; expressed in terms of wave-length instead of frequency, it becomes

$$n^2 - 1 = \frac{3 \cdot 76 \times 10^{-4}}{1 \cdot 378777 - 10^{-10} \lambda^{-2}}. \qquad (23)$$

This means a single dominant wave-length $\lambda_0 = 851 \cdot 6$. Comparing with (21) and (22) we see that λ_0 is a mean value for the lines of the doublet in each case, being roughly equal to $\frac{1}{3}(\lambda_1 + 2\lambda_2)$. A few values calculated from (23) are given in Column 6 of Table I, to show how the differences increase rapidly in the ultra-violet although there may be good agreement over the small range from which the formula was calculated.

In a more elaborate formula due to Lundblad,[*] the hydrogen molecule is supposed to contain two revolving electrons at a distance r apart. The formula is given as

$$\frac{n^2 - 1}{n^2 + 2} = \frac{4\pi N}{3} \cdot \frac{1}{1 - \xi - 2\xi^2} \cdot \frac{2}{H}, \qquad (24)$$

where $\qquad H = m(p_0^2 - p^2)/c^2; \qquad \xi = 1/r^3 H.$

Lundblad uses the accepted electronic value of e/m, and then determines the two remaining constants from Koch's values of the dispersion; his results are

$$p_0^2 = 8 \cdot 20892 \times 10^{32}; \qquad r = 1 \cdot 021 \times 10^{-8} \text{ cm.}$$

Now (24) is in fact of the type we have considered in (5); for, putting the right-hand side into partial fractions, we obtain

$$\frac{n^2 - 1}{n^2 + 2} = \frac{8\pi N e^2}{9m} \left\{ \frac{1}{p_0^2 - 2p_1^2 - p^2} + \frac{2}{p_0^2 + p_1^2 - p^2} \right\}, \qquad (25)$$

where $mp_1^2 = e^2/r^3$. Using the numerical values given above, and expressing in wave-lengths for comparison with (18) and (19), Lundblad's formula becomes

$$\frac{n^2 - 1}{n^2 + 2} = \frac{1 \cdot 605896 \times 10^{-4}}{3} \left\{ \frac{1}{0 \cdot 976725 - 10^{-10} \lambda^{-2}} + \frac{2}{2 \cdot 977210 - 10^{-10} \lambda^{-2}} \right\}. \qquad (26)$$

The calculated values for some wave-lengths are shown in Column 7 of Table I. Although there is good agreement over the range to which Koch's experiments extended, the values become increasingly too large in the extreme ultra-violet. This may be connected with the electronic value of the constant C being assumed in advance, and so leading to too large a separation of the lines of the doublet in (26) compared with those in (18) or (19).

* R. Lundblad, 'Untersuch. über die Optik der disperg. Medien,' p. 192 (Uppsala, 1920).

Debye's dispersion formula* for hydrogen is based definitely on Bohr's model; the methods used have been developed further by Sommerfeld.† Kirn, in the paper already quoted, calculates values of the refractive index from Debye's formula for comparison with his experimental results; these values, as given by Kirn, are shown in Column 8 of Table I. In this case the calculated values fall short of the observed, and increasingly so towards the shorter wave-lengths.

It will be seen that these various formulæ have analogous consequences as regards the scattering of light.

Scattering of Light by Hydrogen.

The quantity determined in Lord Rayleigh's experiment is the ratio of the intensities of the two polarised components of the scattered light when the primary beam is unpolarised; the revised value of this ratio for hydrogen is given as 0·0383.‡ The corresponding formula on the present theory is (13), and we can calculate the value of this over the range of wave-lengths for which the dispersion formula is valid. Before doing so we may review briefly the other dispersion formulæ which were examined in the previous section.

Cuthbertson's formula, interpreted as meaning an isotropic molecule, gives zero value for the ratio (13), and this corresponds with the large defect of the calculated values of the dispersion in the short wave-lengths.

Debye's formula also falls short in the ultra-violet, as we saw in Table I. M. Born, in the papers quoted above, has used Debye's dispersion formula in calculating the ratio of intensities for the scattered light. His method is different from that used here; further his calculations give the ratio as negligibly small, apparently of the order of 10^{-5}.

On the other hand, Lundblad's formula gives a dispersion curve which rises too steeply in the ultra-violet, and so indicates a resonance wave-length which is too large. Since his dispersion formula is of the same type as (18) and (19) we can calculate the ratio of the intensities of the scattered light from (13); the value ranges from 0·1297 at the wave-length 5462 to 0·2175 at the wave-length 1854, and is therefore three or four times as large as the experimental value.

In the calculations for the new formulæ (18) and (19), we have the values of the sub-indices n_1 and n_2, and so the value of the ratio (13) can readily be

* P. Debye, 'Sitzungsber. d. Münch. Akad.,' p. 1 (1914).

† A. Sommerfeld, 'Ann. der Phys.,' vol. 53, p. 497 (1917).

‡ Lord Rayleigh, 'Roy. Soc. Proc.,' A, vol. 97, p. 449 (1920). In Lord Rayleigh's earlier work ('Proceedings,' 1918) the value 0·017 was given for hydrogen; and the same value is adopted by J. Cabannes (Ann. de Physique, 15, 1921) to express his experimental results, which ranged between 0·01 and 0·02.

found over the whole range. Although the expression (13) would require further modification near the resonance wave-lengths, just as in the corresponding dispersion formula, it is of interest to carry the calculations as far as the lines of the doublet in each case. Since $n^2 - 1 = \frac{1}{3}\{n_1{}^2 - 1 + 2(n_2{}^2 - 1)\}$, it follows from (13) that the limiting values of the ratio are $\frac{1}{2}$ and $\frac{3}{4}$ at the lines of the doublet. The calculated values for some wave-lengths are shown in the second and third columns of Table II; the wave-lengths shorter than 1854 are the doublet lines given by (21) and (22).

Table II.—Ratio of Intensities for Hydrogen.

λ.	(18).	(19).
5462	0·0326	0·0353
4359	0·0337	0·0361
3342	0·0358	0·0376
2753	0·0384	0·0394
1854	0·0517	0·0478
984	0·5000	—
924	—	0·2222
781	0·2222	—
699	—	0·5000

The difference between the values for the prolate and oblate types is of interest: the values from (18) begin by being less than those from (19), but they increase more rapidly owing to the larger maximum occurring at the longer wave-length of the doublet.

In comparing these results with Lord Rayleigh's value of 0·0383, it should be remembered that the latter is subject to experimental error (estimated at not more than 5 per cent.); further, the primary light was not monochromatic but was the radiation from an arc light. On the other hand, the calculated values involve possible experimental errors in the dispersion; and in addition the constants of the dispersion formula were not adjusted to give the best average agreement. It may be claimed that there is substantial agreement between the calculated values and experiment; but one could not decide between the alternative dispersion formulæ without more elaborate numerical analysis, and it would also probably need further experimental results. It may be that experiments with fluid or other media may offer less difficulties than in the case of gases to finding the variation of the ratio of intensities with wave-length; and a corresponding extension of the present analysis may be possible, connecting this variation with the dispersion formula of the medium.

On the Stress-optical Effect in Transparent Solids strained beyond the Elastic Limit.

By L. N. G. Filon, M.A., D.Sc., F.R.S., Professor of Applied Mathematics and Mechanics at University College, London, and H. T. Jessop, M.Sc., University College, London.

(Abstract.)

Introduction.

Experiments carried out by one of the present authors with a slab of glass under flexure have indicated that artificial double refraction in glass strained beyond the elastic limit is probably proportional to the stress rather than to the strain.[*] More recently, the experiments of Prof. E. G. Coker and Mr. K. C. Chakko[†] have suggested that in celluloid or xylonite, whilst for the highest loads the double refraction is no longer proportional to either the stress or the strain, it is more nearly proportional to the former than to the latter.

Further, casual observations in the past had shown one of us that, when a piece of transparent material, whether glass or celluloid, which had been overstrained, was released, a certain amount of residual illumination was visible between crossed Nicols in certain cases. The illumination gradually died out, showing that the artificial double refraction exhibited some of the characteristics of permanent set, with a slow recovery. No precise measurements of this effect, however, seem ever to have been made.

In the few isolated cases observed by one of us the stress distribution was a complex one. In such a case the residual optical effect on removal of the load is the consequence of a mechanical readjustment of stresses and is not a true optical residual, that is, a double refraction persisting after the stress has been entirely removed.

It seemed therefore of interest to examine whether, in fact, such optical permanent set did exist, as if so it would apparently settle the question whether stress or strain is the immediate cause of double refraction.

In addition, this opened up the whole question of time effects in this connection, of which apparently no observations had been made to date, and

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[*] *Cf.* L. N. G. Filon, 'Phil. Trans.,' A, vol. 207, pp. 303–305.

[†] "The Stress-Strain Properties of Nitro-Cellulose and the Law of its Optical Behaviour," 'Phil. Trans.,' A, vol. 221, pp. 139–162.

it was hoped that a study of such effects might throw some light on the mechanism of photo-elasticity, of which very little is really known.

The plan adopted was to observe a test-piece under simple stress (pressure in the case of glass and tension in that of xylonite or celluloid) between crossed Nicols. Sodium light was employed throughout and changes of relative retardation were measured by the shift of the black band produced by a Babinet compensator.

In such a case of simple loading the applied stress should disappear throughout immediately the load is removed, *provided the material is homogeneous.*

As the experiments progressed, new lines of enquiry suggested themselves, so that, ultimately, the whole subject of time-effect, or creep, for strain as well as for double refraction, came under consideration, more particularly in xylonite.

Experiments on Glass.

Rectangular blocks of optical glass of specific gravities ranging from 2·76 to 4·78 had been supplied before the War by Messrs. Zeiss, and these specimens were subjected to simple pressure between two knife-edge blocks. The loads applied approached, in most cases, as near to the breaking point as we dared go (150 to 220 kgrm.-wt. per square centimetre), and were left on for a period of 24 hours or more, the relative retardations produced ranging from three wave-lengths for the lighter glasses to one wave-length for the heaviest glass.

The apparatus employed allowed of the load being put on and removed very rapidly and smoothly, the optical effect being observed at the same time, while the retardation could be measured to an accuracy of 0·01 wave-length; but in no case was there any increase in the observed retardation during the time the load was left on, nor was there any trace of residual retardation on removal of the load.

No direct measurement was made of the strain in the glass, as the experimental difficulties in this respect have not yet been overcome, but experiments described elsewhere* indicate that plastic flow in glass sets in at much lesser stresses than those here employed.

So far, then, as these experiments go, there is no indication of any residual stress-optical effect, or that the artificial double refraction in glass at ordinary temperatures is dependent upon any other factor than the stress actually applied.

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* H. T. Jessop, 'Phil. Mag.,' vol. 42, October, 1921.

We next examined xylonite, where residual effects previously observed had been much more marked. In this case the specimens were observed under tension, as pressure could not be applied without causing buckling.

An extensometer was devised which permitted of the observation of simultaneous optical effect and strain, and we found a considerable time-effect in both, under stresses ranging from 67·6 to 236·4 bars.

The specimen was loaded at a given instant, as quickly and smoothly as possible, and timed observations of the stress-optical effect and strain were taken over a given period (generally one hour, though in some cases the observations were continued for several days, after which time the creep was found to have practically ceased). At the end of this period, which we call the "loading" period, and during which the load was kept constant, the load was removed, and timed readings taken during the "unloading" or "recovery" period.

On loading, the observations of both stress-optical effect and strain showed in every case an immediate initial effect, roughly proportional to the load applied, followed by a marked creep. This creep was at first so rapid that no actual reading of the initial effect could be taken, and the value of this initial effect could consequently only be deduced from a graph.

On unloading, a similar immediate effect, followed by creep, was observed. The initial recovery was roughly equal to the initial effect on loading, but in general the rate of creep on recovery was not the same as that on loading. If the load is taken off after many hours, so that the specimen has had time to settle down, both strain and retardation on recovery give a curve identical with the corresponding curve on loading reversed. But if the load is taken off at an earlier stage, both strain and retardation on recovery follow a different law, which depends upon the time during which the original load was maintained. The form of this law has not yet been determined by us.

The optical creep on loading is comparatively large and may easily amount to 10 per cent. of the initial value in a few minutes. This percentage, however, diminishes as the load is decreased. These facts have an important bearing on stress determinations from observations of artificial double refraction in celluloid.

Curves of strain and relative retardation were then plotted to time, and attempts were first made to fit an exponential formula of the type

$$r = \alpha - \beta e^{-kt},$$

this being the law that would be expected, assuming the stresses in the

material to be composed of elastic and viscous parts, obeying Hooke's and Stokes' laws respectively.

A thorough examination of a number of curves, however, showed large and systematic divergences from this law, and it was definitely discarded.

Eventually, after trying many formulæ, including combinations of exponential, logarithm, and power, all of which proved unsuitable for various reasons, we found that the loading curves were very well fitted by formulæ of the type

$$s = s_0 + at^{1/3} + bt \tag{1}$$

for the strain, and

$$r = r_0 + pt^{1/3} + qt \tag{2}$$

for the stress-optical effect.

When the retardation was plotted to simultaneous strain, it was found to give quite a good straight line, leading to the relation

$$r = \alpha \mathrm{T} + \beta s \tag{3}$$

where T is the stress applied to the specimen, α and β being either constant for a given specimen at a given period of its history or, at any rate, slowly varying functions of T.

This law was also found to hold for the values of r and s on unloading, T then being zero in every case.

The values of the constants in formulæ (1), (2), and (3) were found to vary from specimen to specimen, and also to be affected by previous treatment of the specimen and by lapse of time, the variation being such as to indicate a progressive change with time in the physical properties of the xylonite.

On repeating the experiments after about six months, the constants a and p, which measure the bulk of the creep, at any rate in the earlier stages, were found to be practically halved. Thus the importance of using old and well-seasoned specimens in stress investigations cannot be too much emphasised.

The law (3) is satisfactorily explained on the assumption that xylonite is made up of two constituents, one perfectly elastic and the other plastic, the stress-optical effect in each being strictly proportional to the applied stress, but the two components having different stress-optical coefficients.

In order to test whether this heterogeneity were uniformly distributed throughout the material, or whether the two components were provided by an elastic skin enclosing a plastic core, two similar specimens were tested, one specimen having a thickness of 1 mm. removed from each face immediately before loading.

The differences found between the constants α and β for the two specimens were less than many which we had found between different sets of observations on the same specimen.

It would appear, then, that the " skin " and " core " could not produce the effect observed, and that if the two-material hypothesis is correct, then xylonite consists of an intimate mixture of two constituents, with different elastic and plastic properties and different stress-optical coefficients. It is further possible that the two materials are allotropic modifications of the same substance, and that their proportions are altered by the action of stress and other causes. This might account for the observed divergences in the values of α and β under different conditions.

The Rotation of Two Circular Cylinders in a Viscous Fluid.

By G. B. Jeffery, M.A., D.Sc., Fellow of University College, London.

In a previous communication[*] we employed the solution of the equation $\nabla^4 \psi = 0$ in bipolar co-ordinates defined by

$$\alpha + i\beta = \log \frac{x + i(y+a)}{x + i(y-a)} \tag{1}$$

to discuss the problem of the elastic equilibrium of a plate bounded by any two non-concentric circles.

There is a well-known analogy between plain elastic stress and two-dimensional steady motion of a viscous fluid, for which the stream-function satisfies $\nabla^4 \psi = 0$. The boundary conditions are, however, different in the two cases, and the hydrodynamical problem has its own special difficulties.

In this paper we discuss the problem of the rotation of two parallel infinite circular cylinders in a viscous fluid. The solution is different in form according as one cylinder does, or does not, enclose the other. In the former case the problem can be solved in finite terms; while in the latter the problem is in general insoluble; that is to say, except in special circumstances, there is no *steady* motion which satisfies all the necessary conditions.

Let the two cylinders be defined by constant values of α, say, $\alpha = \alpha_1, \alpha_2$. We may take α_1 positive and greater than α_2, then α_2 will be positive or negative according as the second cylinder does, or does not, enclose the first. Let the cylinders rotate about their axes with angular velocities ω_1, ω_2. The stream-function ψ satisfies $\nabla^4 \psi = 0$ when steady motion is established, and

will be an even function of β, single-valued for circuits which enclose either or both of the cylinders. Selecting the appropriate terms from our solution (T21), and re-instating terms explicitly rejected on the ground that they correspond to zero elastic stresses, we have[*]

$$h\psi = A_0 \cosh \alpha + B_0 \alpha \cosh \alpha + C_0 \sinh \alpha + D_0 \alpha \sinh \alpha$$

$$+ (A_1 \cosh 2\alpha + B_1 + C_1 \sinh 2\alpha + D_1 \alpha) \cos \beta$$

$$+ \sum_{n=2}^{\infty} \{A_n \cosh (n+1) \alpha + B_n \cosh (n-1) \alpha + C_n \sinh (n+1) \alpha$$

$$+ D_n \sinh (n-1) \alpha\} \cos n\beta, \quad (2)$$

where $\qquad\qquad\qquad\qquad h = (\cosh \alpha - \cos \beta)/a.$

This solution is subject to the qualification (Tp. 275) that the series *may* converge only for positive or for negative values of α, or in other words, that the expansion of $h\psi$ may be different on opposite sides of the plane $\alpha = 0$.

Since ψ is single-valued it follows that the velocities are single-valued and that the stresses are single-valued if p the mean pressure is so. We can readily calculate p from (2) by noting that $\mu \nabla^2 \psi$ and p are conjugate functions. In this way we find that p contains the many-valued term $(B_0 + D_1)\beta$, so that we must have

$$B_0 + D_1 = 0. \qquad\qquad (3)$$

§ 2. *A cylinder rotating in a viscous fluid contained in a non-concentric cylindrical vessel.* Let the inner cylinder be $\alpha = \alpha_1$ and the containing vessel $\alpha = \alpha_2$, and let their angular velocities ω_1, ω_2 be as shown in fig. 1. If d_1, d_2
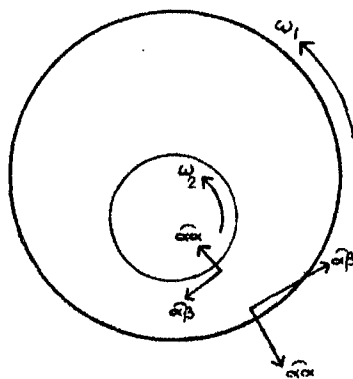
FIG. 1.

[*] Mr. B. Dutt ('Bull. Calcutta Math. Soc.,' vol. 10, p. 43 (1919) has given a solution of $\nabla^4\psi = 0$ in these co-ordinates and a discussion of the problem of the present paper. He, however, omits the terms in $a \cosh a$, $a \sinh a$, $a \cos \beta$, as well as some others which appear in our general solution (T 21). It will appear that these terms play an important part in the solution of our present problem. Moreover, Mr. Dutt takes n of the form half an odd integer, so that the series (2) has a discontinuity on the plane through the axes of the cylinders on part of which β has a discontinuity of 2π.

denote the distances of the centres of the circles α_1, α_2 from the origin, and r_1, r_2 their radii, we have (Tp. 284)

$$r_1 = a \operatorname{cosech} \alpha_1 \qquad r_2 = a \operatorname{cosech} \alpha_2,$$
$$d_1 = a \coth \alpha_1 \qquad d_2 = a \coth \alpha_2. \qquad (4)$$

If the components of fluid velocity in the positive directions of α, β are u_α, u_β, we have

$$u_\alpha = -h \frac{\partial \psi}{\partial \beta} = -\frac{\partial}{\partial \beta}(h\psi) + \frac{\psi}{a} \sin \beta,$$

$$u_\beta = h \frac{\partial \psi}{\partial \alpha} = \frac{\partial}{\partial \alpha}(h\psi) - \frac{\psi}{a} \sinh \alpha, \qquad (5)$$

and from these we obtain the boundary conditions

$$\left. \begin{array}{l} \psi = \psi_1 \\ \dfrac{\partial}{\partial \alpha}(h\psi) = \dfrac{\psi_1}{a} \sinh \alpha_1 - \dfrac{a\omega_1}{\sinh \alpha_1} \end{array} \right\} \text{on } \alpha = \alpha_1 \qquad (6)$$

and

$$\left. \begin{array}{l} \psi = \psi_2 \\ \dfrac{\partial}{\partial \alpha}(h\psi) = \dfrac{\psi_2}{a} \sinh \alpha_2 - \dfrac{a\omega_2}{\sinh \alpha_2} \end{array} \right\} \text{on } \alpha = \alpha_2. \qquad (7)$$

From (2) and (3) we assume

$$h\psi = A_0 \cosh \alpha + B_0 \alpha \cosh \alpha + C_0 \sinh \alpha + D_0 \alpha \sinh \alpha$$
$$+ (A_1 \cosh 2\alpha + B_1 + C_1 \sinh 2\alpha - B_0 \alpha) \cos \beta, \qquad (8)$$

and (5) and (6) then give

$$A_0 \cosh \alpha_1 + B_0 \alpha_1 \cosh \alpha_1 + C_0 \sinh \alpha_1 + D_0 \alpha_1 \sinh \alpha_1 = \cosh \alpha_1 . \psi_1/a,$$

$$A_0 \sinh \alpha_1 + B_0 (\alpha_1 \sinh \alpha_1 + \cosh \alpha_1) + C_0 \cosh \alpha_1$$
$$+ D_0 (\alpha_1 \cosh \alpha_1 + \sinh \alpha_1) = \frac{\psi_1}{a} \sinh \alpha_1 - \frac{a\omega_1}{\sinh \alpha_1},$$

$$A_1 \cosh 2\alpha_1 + B_1 + C_1 \sinh 2\alpha_1 - B_0 \alpha_1 = -\psi_1/a,$$

$$2A_1 \sinh 2\alpha_1 + 2C_1 \cosh 2\alpha_1 - B_0 = 0, \qquad (9)$$

with four precisely similar equations obtained from these by writing α_2, ψ_2, ω_2 for α_1, ψ_1, ω_1 respectively. We have thus eight equations for the seven coefficients and the condition for their consistence will determine $\psi_1 - \psi_2$.

With the usual notation for the stresses,

$$\widehat{\alpha\beta} = \mu \left\{ \frac{\partial}{\partial \alpha} \left(h^2 \frac{\partial \psi}{\partial \alpha} \right) - \frac{\partial}{\partial c} \left(h^2 \frac{\partial \psi}{\partial \beta} \right) \right\}, \qquad (10)$$

where μ is the coefficient of viscosity. On a surface for which α, ψ are constant this reduces to

$$\widehat{\alpha\beta} = \mu h \left\{ \frac{\partial^2}{\partial \alpha^2}(h\psi) - \frac{\psi}{a} \cosh \alpha \right\}. \qquad (11)$$

The couple per unit length which must be applied to the inner cylinder in order to maintain the motion is

$$L_1 = -a \operatorname{cosech} \alpha_1 \int_{-\pi}^{+\pi} \frac{\widehat{\alpha\beta}}{h} \, \alpha\beta$$

and using (11), (8) and the first of equations (9), this reduces to

$$L_1 = -4\pi\mu a \{B_0 + D_0 \coth \alpha_1\}. \tag{12}$$

Similarly the couple which must be applied to the containing vessel is

$$L_2 = 4\pi\mu a \{B_0 + D_0 \coth \alpha_2\}. \tag{13}$$

The couple is in each case reckoned positive in the same sense as the angular velocity.

Solving equations (9) and substituting in (12) and (13), we obtain

$$L_1 = \frac{4\pi\mu a^2 \{(\omega_1 - \omega_2)(\alpha_1 - \alpha_2) \coth(\alpha_1 - \alpha_2) - \omega_1 \sinh \alpha_2 \operatorname{cosech}^2 \alpha_1 \sinh(2\alpha_1 - \alpha_2) + \omega^2\}}{(\alpha_1 - \alpha_2)\{\sinh^2 \alpha_1 + \sinh^2 \alpha_2\} - 2 \sinh \alpha_1 \sinh \alpha_2 \sinh(\alpha_1 - \alpha_2)} \tag{14}$$

and

$$L_2 = -\frac{4\pi\mu a^2 \{(\omega_1 - \omega_2)(\alpha_1 - \alpha_2) \coth(\alpha_1 - \alpha_2) - \omega_1 - \omega_2 \sinh \alpha_1 \operatorname{cosech}^2 \alpha_2 \sinh(\alpha_1 - 2\alpha_2)\}}{(\alpha_1 - \alpha_2)\{\sinh^2 \alpha_1 + \sinh^2 \alpha_2\} - 2 \sinh \alpha_1 \sinh \alpha_2 \sinh(\alpha_1 - \alpha_2)}. \tag{15}$$

These rather complicated formulæ take a very simple form in a special case. If we put $\omega_2 = 0$, $\alpha_2 = 0$, we have the solution for a cylinder rotating in a viscous fluid bounded by an infinite rigid plane parallel to the axis of the cylinder. The couple required to keep the cylinder in motion is obtained from (14). Using (4), we may express this in terms of the radius of the cylinder (r), and the distance of its axis from the plane boundary (d). We obtain

$$L_1 = 4\pi\mu\omega_1 \, r^2 d / \sqrt{(d^2 - r^2)}. \tag{16}$$

Making d tend to infinity, we have the well-known value of the couple necessary to maintain the rotation of a cylinder in an infinite fluid, namely, $4\pi\mu\omega_1 r^2$, per unit length.

§ 3. *The rotation of two cylinders in an infinite viscous fluid.* In this case there is, in general, no steady motion of the fluid for which the velocity of the fluid vanishes at infinity. This may be shown by means of (2) for any radii and angular velocities of the cylinders, if we allow for the difference in the expansions on opposite sides of the plane $\alpha = 0$. But the algebra is heavy and we will confine ourselves to the consideration of a particular case which brings out quite clearly the nature of the difficulty.

Let two equal circular cylinders $\alpha = \pm \alpha_1$ rotate in opposite senses with

angular velocity ω as shown in fig. 2. We may then avoid all difficulties arising from the possibility of different expansions for $h\psi$ according as $\alpha \gtrless 0$
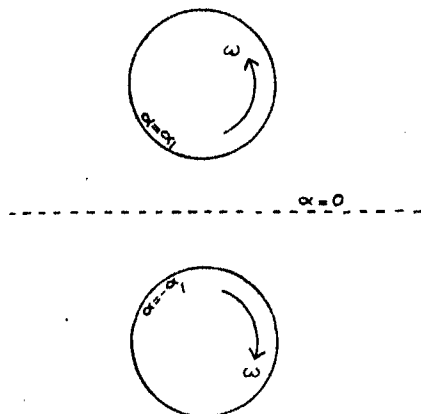
Fig. 2.

by noting that, by symmetry, ψ is a constant and $\widehat{\alpha\beta}$ vanishes on the plane $\alpha = 0$. Using (11), we may take

$$\psi = 0, \qquad \frac{\partial^2 (h\psi)}{\partial \alpha^2} = 0 \qquad (17)$$

on $\alpha = 0$. It may be seen that the most general form of (2) consistent with (17) is

$$h\psi = \mathrm{B}_0 \, \alpha \, (\cosh \alpha - \cos \beta) + \mathrm{C}_0 \sinh \alpha + \mathrm{C}_1 \sinh 2\alpha \cos \beta. \qquad (18)$$

The boundary conditions (6) give four equations to determine $\mathrm{B}_0, \mathrm{C}_0, \mathrm{C}_1, \psi_1$. They are consistent and they give

$$\mathrm{B}_0 = -\frac{a\omega \cosh 2\alpha_1}{2 \cosh \alpha_1 \sinh^3 \alpha_1}, \quad \mathrm{C}_0 = \frac{a\omega \cosh \alpha_1}{2 \sinh^3 \alpha_1}, \quad \mathrm{C}_1 = -\frac{a\omega}{4 \cosh \alpha_1 \sinh^3 \alpha_1}.$$

At infinity $(\alpha, \beta = 0)$, we have from (5)

$$u_\alpha = 0$$

$$u_\beta = \mathrm{C}_0 + 2\mathrm{C}_1 = \frac{a\omega}{2 \cosh \alpha_1 \sinh \alpha_1},$$

so that, if r is the radius of either cylinder and d is the distance apart of their axes, we see using (4) that the fluid at a distance from the cylinders is moving in uniform stream motion with velocity V in a direction perpendicular to the plane containing the axes, where

$$\mathrm{V} = r^2 \omega / d. \qquad (19)$$

The above demonstration is open to the criticism that in obtaining (18) we have assumed that (2) is absolutely and uniformly convergent *on the plane*

$\alpha = 0$, which may possibly be the boundary of its region of convergence. This difficulty may be avoided and some further light thrown upon the physical nature of the problem by proceeding as follows: we can uniquely determine ψ in the form (8) so that it satisfies the boundary conditions (6) on $\alpha = \alpha_1$ and (17) on $\alpha = \alpha_2$, where α_2 is positive. This would correspond to the stream-function due to a cylinder rotating in a viscous fluid contained in a non-concentric cylindrical vessel whose inner surface is smooth and incapable of exerting any tangential traction on the fluid. This problem admits of a unique solution. Now make α_2 tend to zero so that the radius of the containing vessel becomes very large. It will be found that the motion of the fluid in those parts of the vessel which are remote from the rotating cylinder does not tend to zero, but in fact tends to the motion described by (19).

The kinetic energy of the motion is clearly infinite while the couple on the cylinder is easily seen to be finite. It follows that the motion could not be set up in any finite time. No steady motion will ever be reached, and the longer the cylinders have been rotating the greater the mass of fluid which is set in motion.

This result is not surprising. By a well-known result due to Stokes, the motion of a viscous fluid due to a single circular cylinder moving through it with a velocity of translation never attains to a steady state. And our present problem is very similar to that of Stokes. Both are concerned with " doublet " motions, in which fluid is forced out in one direction and drawn in in the opposite direction.

The Catalytic Activity of Copper—Part III.

By W. G. Palmer, St. John's College, Cambridge.

The catalytic action of the metallic oxides upon alcohols has been very completely studied by Sabatier and Mailhe[*] in the qualitative way. They showed that the alcohols in contact with oxides at 200°—400° C. can undergo two sorts of decomposition—(a) dehydration, (b) dehydrogenation —and they were able to classify oxides in respect of these two reactions. The following Table is extracted from their paper, and includes only oxides the activity of which is preferentially dehydrogenating:—

	Activity (ethyl alcohol, at 340-350° C.).	Composition of gaseous product.	
		Ethylene.	Hydrogen.
		volume per cent.	volume per cent.
Ferric oxide	32	14	86
Zinc oxide	6	5	95
Manganous oxide	3·5	0	100
Magnesium oxide	Traces only	0	100
Copper reduced from cupric oxide.	110	0	100

The activity is expressed in arbitrary units.

Only the oxides at the extreme ends of the list given by Sabatier bring about one reaction exclusively. For example, thoria is exclusively dehydrating, and magnesia is the only exclusively dehydrogenating oxide. However, the dehydrating activity of the above oxides is small.

The present communication describes the effect upon the catalytic (dehydrogenating) activity of copper, of admixing these oxides in varying proportions. The effect of volatile additions, such as hydrogen and water vapour, has been previously described.[†]

Apparatus, and Preparation of the Catalyst.

It was convenient in the present work to use a smaller catalytic surface than previously, and hence a gas-meter working with smaller quantities of

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[*] 'Ann. de Chim. et Phys.,' vol. 21, p. 289 (1910).
[†] 'Roy. Soc. Proc.,' A, vol. 98, p. 13 ; vol. 99, p. 412.

gas was necessary. The diagram (fig. 1) shows the form of meter found to give satisfactory results.
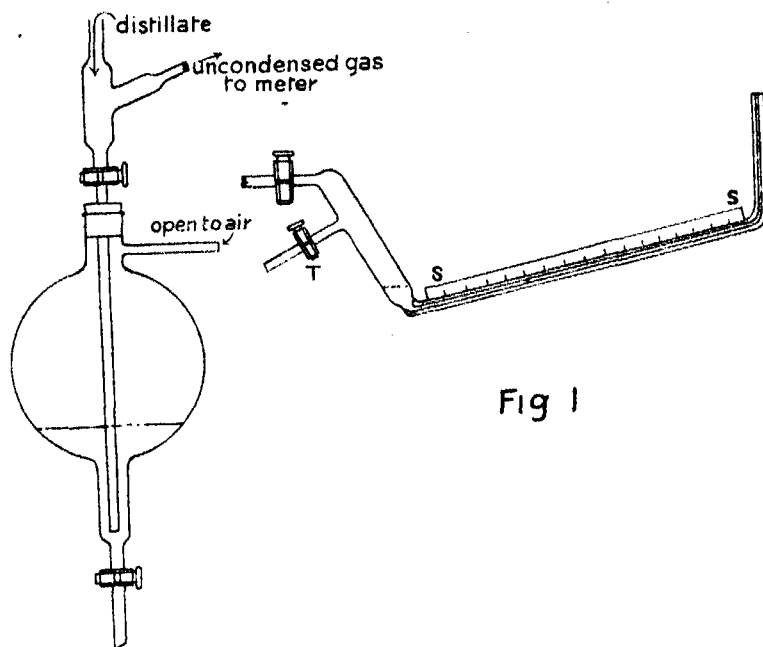
Fig 1

In order to give a motion of about 2 cm. on the scale SS, an evolution of about 0·2 c.c. of gas was required. The increase of pressure in the apparatus consequent upon this motion was too slight to cause an appreciable change in the rate of boiling of the alcohol below the reaction tube. The mode of working consisted in depressing the chronograph key, and simultaneously opening the tap, T, for a moment, when 2 cm. of the scale had been covered by the liquid. The liquid then fell back to its zero position, and a new reading was taken, and so on. If the capillary tube is kept clean the motion of the liquid is quite regular. This meter replaced the "bubbler" formerly used. The one-litre flask for temperature control was retained between the meter and the rest of the apparatus. The use of this sensitive gauge makes it impossible to allow the condensed alcohol to remain in the system of the apparatus, as the increasing volume of the distillate would be registered as a gas evolution. A special receiver (see fig. 1) was devised to meet this difficulty.

A fresh sample of ethyl alcohol taken from a large stock of 3 litres was used for each activity test. The amount necessary for one test (70 c.c.) was boiled vigorously for 2 hours to expel dissolved air, in an apparatus directly connected with the boiler supplying alcohol vapour to the reaction

tube. The hot alcohol was run in through a tap immediately before a test was begun. A constant current was used throughout for the heating coil in the boiler.

The reduction of the catalyst was carried out with carbon monoxide, it having been previously shown (*loc. cit.*) that other reducing agents complicate the catalytic effect of the reduced copper. A carbon monoxide generator, in which the gas was made by mixing concentrated sulphuric and formic acids at 60° C., was directly connected with the reaction tube. The gas passed over soda-lime and calcium chloride before being admitted to the main apparatus.

After many experiments all methods of preparing the contact material by impregnation of porous rods from solution were abandoned. In the former work with pure copper the catalyst surface was made by impregnating gas-mantle supports in an aqueous solution of copper formate, drying, and then igniting to oxide at 250° C. This method is not satisfactory for the study of mixed catalysts, since it is practically impossible to choose conditions that prevent a separation (owing to differential surface action) of the constituents of the mixture on drying.

For example, a porous rod was soaked in an ammoniacal solution of copper formate and silver oxalate, in which the ratio Cu/Ag was 100/5. After drying and ignition at 250° C., the black deposit was dissolved in hot dilute nitric acid. Only traces of cloudiness were produced in the solution by the addition of ammonium chloride. On breaking the cleaned rod a black ring of silver was discovered below the surface of the rod, showing clearly that the silver oxalate had retreated from the copper during the drying. The following method gives complete control over the composition of the catalytic deposit, and at the same time allows the catalyst to be out of contact with the material of the rod.

About 20 c.c. of a solution of copper sulphate (containing about 10 grm. of the hydrated salt in 100 c.c. of solution) were mixed with a quantity of a solution of the sulphate, or other soluble salt of the metal whose oxide is to be mixed with the copper. The mixed solution was then run from a burette slowly into 100 c.c. of vigorously boiling 10 per cent. sodium carbonate solution. Cupric oxide, mixed with the oxide or carbonate of the added metal, was at once precipitated. In the excess of hot sodium carbonate solution used there remains throughout the precipitation substantially a constant concentration of hydroxide formed by hydrolysis. Sodium carbonate was therefore an advantage over hydroxide solution in providing more uniform conditions of precipitation.

The precipitate was collected on a filter and washed until a small portion

held on a clean platinum wire gave no yellow colour to the Bunsen flame. The washing was in most cases laborious, and was best accomplished by boiling in portions of fresh water and not by washing on the filter-paper. Oxides such as magnesia and zinc oxide, wash out, and it is consequently not easy to predict with exactness the composition of the final oxide mixture from the proportions of solutions taken. Mixtures free from sodium, and containing by weight more than 10 per cent. of magnesia, or 8 per cent. of zinc oxide, could not be prepared owing to this leaching during the washing. The oxide mixtures were finally dried in the steam-oven and analysed by the usual methods.

A mantle-rod, as previously used for supporting the catalyst (*loc. cit.*), was cleaned by ignition, cooled and moistened with pure oleic acid. A sample of mixed oxide was then applied to the rod by rubbing with a soft rag, the fork of the rod serving as a convenient handle. The rod was then ignited to low redness by passing through a Bunsen flame in such a position that, within the flame, the cupric oxide is reduced to metal, and on emerging from the flame is re-oxidised to black oxide. By this means silver and bismuth were given an opportunity to become alloyed with the copper, while non-reducible oxides, such as magnesia and zinc oxide, form saturated solutions in the metal; iron and manganous oxides become re-oxidised with the copper on passing out of the flame.

After cooling, the oleic acid treatment was repeated, until the rod was quite black with the closely-adhering copper oxide. The rod was fully charged, as a rule, after three treatments. Full charge was easily demonstrated by testing the activity, and then re-treating. In no case was the activity increased by more than 2 per cent. by re-treatment after three initial treatments.

To test the reproducibility of the material two rods were prepared, each charged fully with pure copper oxide. Both rods gave the same activity to within 3 per cent. The oleic acid gave no ash on ignition in air.

The deposit consisted of a comparatively thick film, and there is no doubt that the outer layer was not in contact with the material of the rod; the mixture was therefore virtually "unsupported." The rod so prepared was used for each test in place of the eight rods formerly used. It is easy to arrange a single rod centrally in the reaction tube and so secure a minimum amount of eddying in the flow of the vapour. The average amount of copper on each rod was 0·002 grm.

Before an experiment the whole apparatus, up to the gas-meter, was tested tight to a reduced pressure of 60 cm. of mercury, and then filled with nitrogen as in previous work. The temperature in the reaction tube was then raised and kept steady at $205 \pm 1°C.$, while carbon monoxide was passed through the reaction tube for some minutes. The temperature was then raised again and

kept constant during the activity test, the hot alcohol being run into the boiler immediately before the reaction temperature of 260° C. was reached.

The chronograph record started in all cases from the time when the first drop of distillate appeared in the condenser, and continued for a period of 45 to 60 minutes. The activity, in most cases, was quite constant for 25 to 30 minutes, after which it slowly decayed, owing, undoubtedly, to sintering of the catalytic surface. This somewhat rapid onset of decay is the only disadvantage in using catalytic material prepared in the manner described.

The detailed results are now given under separate headings for each mixture. The activities, in all cases, are for reduction by carbon monoxide at 205° C., and reaction with ethyl alcohol at 260° C. They are expressed in arbitrary units by dividing 100 by the distances between marks on the chronograph record. In the following Tables the activities at constant intervals during the period of observation are recorded.

The proportions of oxide are calculated in molecules of oxide to 100 atoms of copper. For this purpose the copper is taken as monatomic, and the oxide given its simplest formula.

1. *Copper—Sodium Carbonate Mixtures.*

It was thought advisable to investigate the effect of leaving small quantities of the precipitant in the prepared oxide.

Three preparations were made under the same conditions as for oxide mixtures :—

(1) Oxide washed once with cold water ; contained 2·8 per cent. sodium carbonate.

(2) Oxide washed five times on the filter-paper with hot water ; contained 0·8 per cent. sodium carbonate.

(3) The oxide was washed quite free from sodium salts (this preparation gave the comparison activity of pure copper).

The sodium salts were estimated by depositing the bulk of the copper electrolytically, the last traces being then removed by hydrogen sulphide, and the liquid evaporated to dryness. The residue was weighed as Na_2SO_4 after treatment with ammonium carbonate in the usual way.

To 100 Cu, 0·5 Na_2CO_3.	1·6 Na_2CO_3.	Pure copper.
	12·0	44·5
	12·5	45·5
No activity	12·5	47·0
(nor with isopropyl alcohol)	12·5	44·5
	12·7	44·7

The drastic effect of small quantities of sodium salts on the copper recalls a similar action on precipitated alumina when this is used as a dehydrating agent for the preparation of ethylene from alcohol.* No doubt the effect originates in the same cause in both cases.

2. *Copper—Magnesium Oxide.*

To 100 Cu, 1·58 MgO.	2·4 MgO.	7·8 MgO.	12·4 MgO.	15·5 MgO.
6·0	39·5	58	75·0	120·0
4·7	38·0	58	77·0	119·5
4·6	41·0	55	76·0	117·0
3·5	40·8	56	79·0	121·0
	40·0		74·0	114·0
	40·7			

3. *Copper—Ferric Oxide.*

To 100 Cu, 1·02 Fe₂O₃.	3·75 Fe₂O₃.	6·6 Fe₂O₃.	20·4 Fe₂O₃.
12·8	9·9	17·0	13·0
12·0	10·0	17·0	14·0
12·4	10·1	16·0	13·2
13·0			13·0
12·5			

4. *Copper—Zinc Oxide.*

To 100 Cu, traces of ZnO.	0·77 ZnO.	2·06 ZnO.	4·65 ZnO.
		24·5	27·0
		28·0	26·5
About 1·0	No activity	26·0	28·0
		27·5	27·0
		27·0	27·5

5. *Copper—Manganous Oxide.*

To 100 Cu, 0·42 MnO.	0·89 MnO.	1·6 MnO.	8·2 MnO.	18·8 MnO.	33·0 MnO.
29·0	84·0	51·0	57	52·5	64·1
27·0	72·0	52·0	55	53·0	63·8
30·0	62·0	51·5	50	53·0	65·0
28·0	58·0	51·0	54		64·5
29·0	55·0				
	47·5				
	48·0				

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* Senderens, 'Ann. de Chim. et Phys.,' vol. 25, p. 476 (1912).

The following Tables show the mean activity calculated from the preceding Tables, and the activity corrected for the dilution of the copper. For this purpose the following specific gravities were used—

Cupric oxide	6·35
Magnesia	3·19
Zinc oxide	5·6
Ferric oxide	5·17
Manganous oxide	5·10

Composition of catalyst.	Mean activity.	Duration of constant activity in minutes.	Corrected activity.
(To 100 Cu)			
MgO 1·58	4–5	(Recorded for 25 minutes)	4–5
2·4	40·0	29	41·0
7·8	55·0	26	59·0
12·4	77·0	30	86·0
15·5	121·0	26	140·0
ZnO traces	1·0	....	1·0
0·77	inactive	...	—
2·06	25·0	25	25·5
4·65	28·0	30	29·5
Fe₂O₃ 1·02	12·6	27	12·6
3·75	10·5	17	11·6
6·6	17·8	15	21·0
20·4	13·0	23	20·0
MnO 0·42	30·0	30	30·0
0·89	84·0–47·5	unstable	—
1·60	51·5	19	52·5
8·2	54·0	26	60·0
16·6	56·5	35	68·0
33·0	64·0	53	92·5
Na₂CO₃ 0·5	inactive	....	—
1·6	12·5	26	12·5
Pure copper	.....	—	45·5

These results are shown graphically in figs. 2 and 3: fig. 3 shows the relation of activity to percentage of oxide on a larger scale for small additions of oxide.

The mixtures containing manganese oxide were precipitated from mixed solutions of cupric and manganous sulphates. After ignition to low redness on the rod the manganese is present as manganic oxide, Mn_2O_3.[*]

The effect of carbon monoxide on this oxide of manganese and on ferric oxide, when each is mixed with cupric oxide, was ascertained in separate experiments.

[*] R. J. Meyer and K. Retgers, ' Zeit. anorg. Chem.,' vol. 57, p. 104.

Fig 2

Fig 3
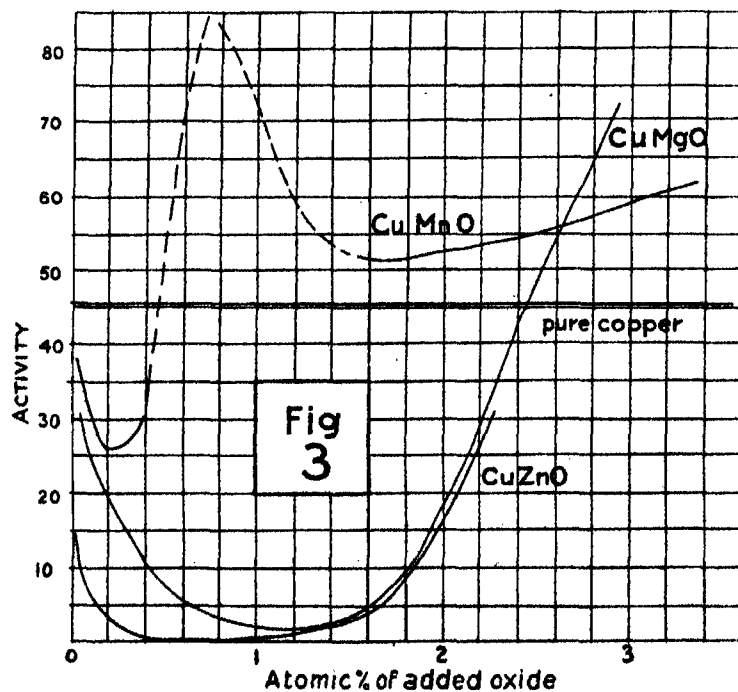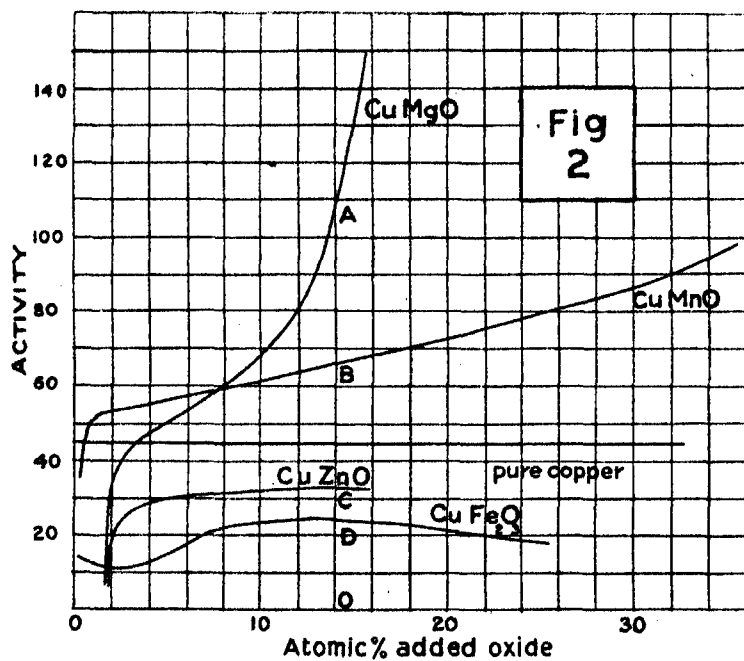
A mixture prepared in the same way as for activity tests was ignited to redness in air, and carbon monoxide was then passed over the mixture contained in a weighed glass tube kept at 205° C. After 1 hour practically no carbon dioxide was leaving the tube, which was then cooled while the gas continued to pass and finally sealed off and re-weighed.

The following results were obtained:—

0·484 of mixed cupric and ferric oxides, containing 29·5 per cent. Fe_2O_3 and 70 per cent. CuO (estimated separately) lost 0·0745 grm. on reduction. Per cent. ' loss = 15·4. Calculated loss for reduction of cupric oxide alone = 14·5.

There appears, therefore, to be only a slight reduction of ferric oxide at the temperature used for reductions.

0·239 grm. of mixed manganic and cupric oxides containing 66·2 per cent. CuO and 33·1 per cent. Mn_2O_3 (estimated separately) lost 0·0395 grm. on reduction. Per cent. loss = 16·5. Calculated for reduction of copper oxide alone 13·6 per cent.; and for manganic oxide to manganous oxide 3·3 per cent.; total loss 16·9 per cent.

Therefore the conditions used for reduction of the copper oxide produce manganous oxide.

If heated in a rapid stream of inert gas, magnesium carbonate is completely decomposed at 200° C.,[*] so that it is extremely improbable that the magnesia in the mixtures retains the carbon dioxide formed by the reduction of the copper oxide. *A fortiori* the other less basic oxides used are not likely to be converted into carbonates.

As will be emphasised in the following discussion, considerable importance attaches to the solubility of the material added to the copper in this metal. Hence the activity of preparations containing a metal known to be soluble in the copper was tested. The metals silver and bismuth were chosen, as these have oxides readily reducible by carbon monoxide at 205° C. The alloys examined had the following compositions (in atomic percentage):—

	Copper-silver Ag		Copper-bismuth Bi
(1)	0·30	....	0·345
(2)	0·375	....	0·57
(3)	0·52	....	0·88
(4)	1·58	....	4·00

With the exception of the mixture of Bi-content, 0·345 per cent., which showed very feeble activity, all of these alloys were completely inactive. Kursanow[†] has shown that silver may give solid solutions in copper up to

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[*] Abegg and Auerbach, 'Handbuch d. anorg. Chem.,' vol. 2 (ii), p. 67.

[†] 'Zeit. anorg. Chem.,' vol. 68, vol. 123 (1910).

4 per cent. of silver, while K. Jeriomin[*] has indicated that bismuth can be present as solid solution up to 0·5 per cent.

The above experiments indicate the drastic nature of the effect of solutes on the activity of the copper. Sabatier and Mailhe (*loc. cit.*) found bismuth to be quite inactive upon primary alcohols.

Discussion of Results—the Properties of "Promotors."

The list of oxides previously given shows that the activity of the pure oxides is usually much less than that of copper. Ferric oxide has the greatest activity, which is only about one-third of that of copper. The oxides, therefore, must be deficient either in adsorbing power or in density of radiation of about $1·0\ \mu$ wave-length (see previous papers, *loc. cit.*).

It is known, however, that oxides such as magnesia, alumina, and ferric oxide adsorb water, and therefore probably alcohol, to a markedly greater extent than metals. We may therefore assume that infra-red radiation of appropriate wave-length is emitted by the oxides only to a slight degree compared with copper. In short, the order of the oxides in the list is one of decreasing emissivity for wave-lengths about $1\ \mu$, and therefore one also of decreasing adsorbing power for this wave-length.

Hence, if a nucleus of copper be surrounded by a *thin* layer of one of these oxides, the adsorbing power of the complex will probably be greater than that of the copper alone, but this favourable increase may be more than counterbalanced by the opacity of the oxide film to the radiation from the copper core. As the proportion of oxide added is increased, the number of copper nuclei will tend to increase; in other words, the oxide peptises the copper. This peptising action will have the effect of keeping the film of oxide thin over a wide range of concentration of the oxide.

The requirements of a "promotor" are thus seen to be : (1) transparency to the radiation from the main catalyst; (2) higher adsorbing power than the main catalyst. A higher peptizing power is an advantage, though it is not essential. Of the oxides examined in the present work, only magnesia and manganous oxides satisfy these requirements.

If, as is quite probable, the same atomic concentration of copper in any oxide implies approximately the same degree of dispersion (in the colloidal sense), then the right-hand portions of the curves (fig. 2) will be in the order of the transparency of the oxides to the copper radiation. These transparencies are measured, in fact, approximately by the ordinates AO, BO, CO, etc.

It will be noticed that the order of activity as given by Sabatier, which is

[*] 'Zeit. anorg. Chem.,' vol. 55, p. 413 (1907).

assumed to be also an order of decreasing adsorption of the proper radiation, is followed in the inverse way by these ordinates. Data on the transparency of metallic oxides to infra-red radiation are scanty, but Königsberger[*] found the following transmission ratios $= \dfrac{\text{(energy incident)}}{\text{(energy transmitted)}}$ for 0.5—4.0 μ.

Ferric oxide..	0·101
Manganite (presumably $MnO(OH)$)	0·160

These results are of the same order as the ratios of the ordinates for ferric and manganous oxides in the curves given above.

The Activity with very low Concentration of Oxide.

When cupric oxide containing about 1 per cent. or less of another oxide is reduced to metal it is possible that the oxide remains dissolved in the metallic copper, and does not separate to form a second phase.

The form of the solution may be " true " or colloidal,[†] but in either case the surface energy of the copper will be diminished by the solute, just as in the case of silver and bismuth admixtures, and adsorption correspondingly reduced.

It is not easy to demonstrate a diminished adsorption for alcohol, but the reduced adsorption for atmospheric oxygen in the case of these preparations was strikingly shown in the following way. In all cases the catalytic preparations were allowed to remain in the reaction tube until this was cold, the exit taps being open and air admitted. While, in these circumstances, an active preparation was always much tarnished, and even blackened deeply by oxidation, an inactive preparation remained quite bright and untarnished, and in general could only be oxidised at room temperature by several days' exposure. The preparations of lowest oxide-content in magnesia, zinc oxide, and manganous oxide, as well as all the silver and bismuth preparations, all showed similar behaviour. Photographs of these preparations are given in fig. 4.

According to the above discussion the curves (figs. 2 and 3) can be interpreted as follows :—

(a) *Ferric Oxide-Copper.*—Oxide quite insoluble in metal, but very opaque to its radiation. Activity of mixtures increased beyond 3·5 per cent. of ferric oxide owing to peptization of the metal.[‡]

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[*] 'Phys. Zeit.,' vol. 4, p. 495 (1904).

[†] For a discussion on the solubility of oxides in copper, see 'Journ. of the Inst. of Metals,' vol. 8 (2), pp. 222, 248 (1912).

[‡] Sabatier and Mailhe found that ferric-oxide reduced the dehydrating activity of alumina very markedly ('Ann. de Chim. et Phys.,' vol. 20, p. 300 (1910)).
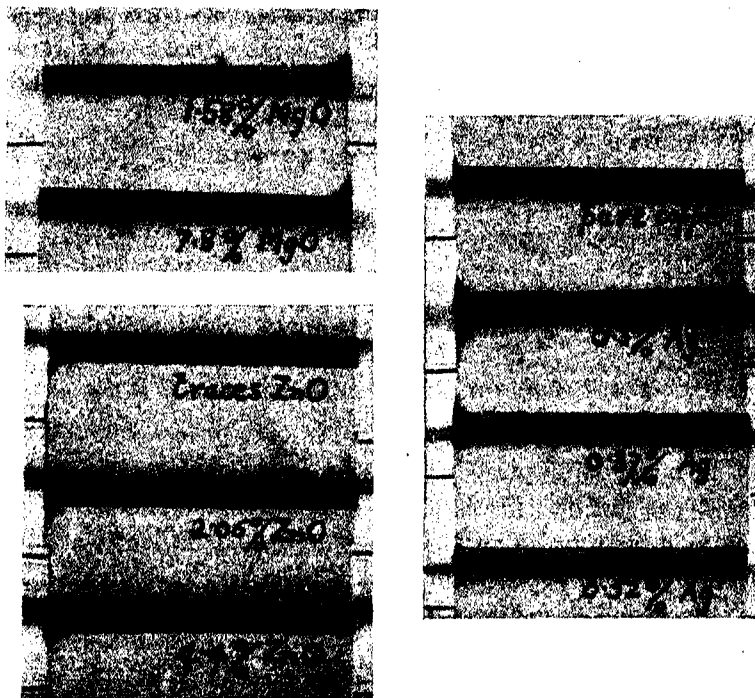
Fig. 4.

(b) *Zinc Oxide-Copper.*—Oxide soluble up to 0·5 per cent. Amounts of zinc oxide from traces up to 0·5 per cent. destroy the activity, which is gradually regained with increasing oxide-content, owing to the formation of two phases. The activity is throughout, however, lower than that of pure copper.

(c) *Manganous Oxide-Copper.*—Oxide only very slightly soluble. The peak at 0·8 per cent. remains unexplained. The value of the activity of this concentration was very unstable, falling from 84 to 47·5 in 17 minutes. Manganous oxide is a weak " promotor " at all concentrations greater than 1 per cent.

(d) *Magnesium Oxide-Copper.*—Oxide soluble up to 1·1 per cent. The oxide is a strong promotor at all concentrations greater than 2·5 per cent.

It is to be noticed that the activities of mixtures, the concentrations of which lie on the steep parts of the curves, are all more or less short lived.

The Spectrum of Beryllium Fluoride.

By Snehamoy Datta, M.Sc. (Calcutta), D.I.C., Research Student, Imperial College of Science.

[Plate 3.]

1. *Introductory.*

In a previous communication,* an account was given of an investigation of the spectra of the fluorides of magnesium, calcium, strontium, and barium, which was undertaken with a view to determine the numerical relations existing between these spectra. It was shown that the homologous series of the different spectra can be connected by empirical equations, involving only the constants of the series equations and the molecular weights or the molecular numbers of the respective compounds. It therefore seemed desirable to extend the investigation in order to ascertain if these relations are maintained in the spectrum of beryllium fluoride. Unlike the other alkaline earth compounds, the spectra of compounds of beryllium have previously received but little attention, and it has even remained doubtful† whether the well-known groups of bands between $\lambda\, 4426$ and $\lambda\, 5446$ belong to the element itself or to the oxide. The present investigation has special reference to the spectrum of beryllium fluoride, which has not previously been recorded.

2. *Experimental.*

Photographs of the spectrum were taken with a 10-feet concave grating, and also with a quartz spectrograph of considerable dispersion (about 5·6 A. per millimetre at $\lambda\, 2900$). The source of light was an ordinary carbon arc fed with beryllium potassium fluoride, this being the only salt in which BeF_2 was available. The presence of potassium does not interfere with the band spectrum of BeF_2, as was proved by a photograph of the spectrum of the arc when fed with potassium fluoride only. In order to distinguish the bands of the fluoride from those of the oxide, direct comparison spectrograms of BeF_2 and BeO_2 were prepared. Fortunately, BeO_2 does not present any spectrum in the vicinity of the fluoride bands. The bands in question can therefore be safely attributed to the fluoride.

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* 'Roy. Soc. Proc.,' A, vol. 99, p. 436.

† H. Kayser, 'Handbuch der Spectroscopie,' vol. 5, p. 162.

As before, the arc was extended to a flame by admixture of sodium carbonate, and only the outer edge of its image was thrown upon the slit. Measurements of the spectrograms were made in the usual way with an iron comparison, using the wave-lengths of the iron lines as given in Burns' Table. The wave-lengths of the band heads have been determined independently from the spectrograms obtained with the concave grating in the second order and the quartz spectrograph. The means of the two concordant sets have been adopted.

3. *Results.*

In the region investigated, namely, between $\lambda\,2200$ and $\lambda\,6700$, BeF_2 presents six groups of bands. These are all in the ultra-violet, as is to be expected on account of the small molecular weight, and all fade off towards the red (see Plate 3). Proceeding towards the long wave-length side, each of the first four groups consists of alternating bright and faint heads, and the bright one is resolved into two heads under high dispersion. In the fifth group the corresponding faint series is missing. In the sixth group seven heads have been accurately measured, but they could not be arranged in series similar to the others. The second, third, and fourth groups are the most intense. The nomenclature adopted is that previously used for the groups of MgF_2 of similar structure. The six groups are thus denominated as E_1, E_2, E_3, E_4, E_5, and E_6. Details of the measurements are given in Table I, which also shows the differences $(O - C)$ between the observed wave-numbers and those calculated from equations of the type

$$\nu = a - bm - cm^2.$$

4. *Structure of the Band $\lambda\,3009{\cdot}85$.*

As all the bands appeared to be of similar structure, the most intense one at $\lambda\,3009{\cdot}85$ was selected for a more detailed investigation. This was photographed in the third order of the grating, giving resolution and definition permitting a satisfactory study of the structure of the band. It was then observed that of the close pair of heads, the outer one on the more refrangible side consists of a single line followed by an apparently continuous spectrum stretching across the interval between the pair. The second head is associated with a series of fine lines, all of which, with the exception of the one next to the head itself, were clearly separated, and could therefore be accurately measured. Starting from the head, the distance from line to line gradually increases, the rate of increase being fairly uniform up to $m = 7$, and subsequently decreasing for the next two members. The lines are fairly sharp to start with, as such lines usually are, but with increasing values of m they

Table I.—Bands of Beryllium Fluoride.

Series.	m.	λ I.A. (air).	$\nu_{obs.}$ (vac.).	$\nu_{obs.} - \nu_{cal.}$
	0	2815·95	35501·66	0·00
	1	26·20	372·81	−0·03
	2	36·31	246·76	+1·18
	3	46·55	120·01	+0·13
E_1	4	56·65	34995·87	+0·13
	5	66·66	873·58	+0·42
	6	76·68	752·15	+0·21
	7	86·59	632·75	+0·07
	8	96·90	510·72	−4·06
	0	2816·33	35496·87	0·00
	1	26·53	368·67	+0·02
	2	36·69	242·05	+0·06
E_1'	3	46·78	117·04	+0·15
	4	56·86	34993·20	−0·06
	5	66·87	871·03	−0·34
	6	76·86	749·97	−0·98
	0	2818·26	35472·44	0·00
	1	28·41	345·18	+0·04
	2	38·61	218·21	−0·23
E_1''	3	48·78	092·39	−0·05
	4	59·02	34966·74	−0·10
	5	69·36	840·78	−1·16
	6	79·48	718·37	+0·73
	0	2908·94	34366·73	0·00
	1	18·39	255·49	0·00
E_2	2	27·77	145·78	+0·01
	3	37·07	037·69	+0·12
	4	46·33	33930·89	−0·27
	5	55·69	825·49	−0·24
	0	2909·32	34362·25	0·00
	1	18·74	251·27	+0·06
E_2'	2	28·09	142·07	−0·12
	3	37·28	035·14	+0·25
	0	2911·80	34333·00	0·00
	1	20·99	225·01	0·00
E_2''	2	30·13	118·17	+0·13
	3	39·18	013·15	+0·06
	0	3009·58	33217·51	0·00
	1	17·97	125·20	0·00
E_3	2	26·40	032·96	−0·04
	3	34·88	82940·68	0·00
	0	3009·85	33214·65	0·00
	1	18·34	121·25	0·00
E_3'	2	26·86	027·93	−0·04
	3	35·41	32934·82	+0·01
	0	3012·99	33180·04	
	1	20·34	099·32	
E_3''	2	—	rather hazy	
	3	—	"	

Table I—(continued).

Series.	m.	λ I.A. (air).	νobs. (vac.).	νobs. − νcal.
	0	3126·06	31979·95	0·00
	1	·33·44	904·64	0·00
	2	40·78	830·10	+0·09
	3	48·09	756·11	+0·05
	4	55·37	682·79	+0·07
E₄	5	62·38	610·56	+0·86
	6	69·84	538·28	−0·01
	7	76·99	467·32	+0·26
	8	84·15	396·58	+0·15
	9	91·28	326·36	−0·89
	10	98·84	257·22	−0·28
	0	3126·35	31976·88	0·00
	1	33·72	901·80	0·00
	2	41·05	827·26	+0·02
E₄′	3	48·42	752·79	−0·41
	4	55·71	679·46	−0·22
	5	62·98	606·66	−0·02
	6	70·22	534·50	+0·30
	7	77·46	462·57	+0·83
	0	3130·79	31931·64	0·00
	1	38·00	858·29	−0·05
	2	45·19	785·39	−0·05
E₄″	3	52·40	712·71	−0·23
	4	59·70	639·46	−0·38
	5	66·69	569·64	+0·50
	6	73·89	498·05	+0·21
	7	81·06	426·97	+0·03
	0	3249·24	30767·61	0·00
	1	55·26	710·64	+0·08
	2	61·28	653·97	0·00
	3	67·30	597·50	−0·05
	4	73·26	541·89	−0·75
	5	79·27	485·86	−0·83
	6	85·27	430·14	−1·02
E₅	7	91·86	373·90	−0·48
	8	97·42	318·01	−0·09
	9	303·50	262·22	0·00
	10	09·40	208·28	−0·75
	11	15·54	152·86	+0·27
	12	21·65	096·91	+1·04
	13	27·75	041·76	+1·70
	14	33·93	29986·09	+2·09
	0	3249·40	30766·10	0·00
	1	55·45	708·84	−0·03
	2	61·50	651·90	0·00
	3	67·50	595·68	−0·26
	4	73·47	539·86	−0·68
	5	79·44	484·28	−0·82
E₅′	6	85·43	428·71	−0·68
	7	91·86	373·90	−0·81
	8	97·38	318·47	0·00
	9	03·37	263·60	+0·64
	10	08·25	208·78	+1·60
	11	15·88	154·09	+2·82

Table I.—*(continued).*

Group.	λ I.A.	ν (vac.).	Group.	λ I.A.	ν (vac.).
E₆	3344 ·12 49 ·93 61 ·56 63 ·67	29894 ·66 842 ·82 739 ·60 720 ·96	E₆	3371 ·26 78 ·03 92 ·59	29654 ·05 594 ·55 467 ·58

Constants for calculation of the series are collected in Table II.

Table II.

Series.	$a = \nu_0.$	b.	c.
E₁	35501 ·66	+ 129 ·6	− 0 ·78
E₁′	35496 ·87	+ 129 ·0	− 0 ·78
E₁″	35472 ·44	+ 127 ·6	− 0 ·30
E₂	34366 ·73	+ 112 ·0	− 0 ·76
E₂′	34362 ·25	+ 112 ·0	− 0 ·96
E₂″	34333 ·00	+ 108 ·5	− 0 ·51
E₃	33217 ·51	+ 92 ·326	− 0 ·016
E₃′	33214 ·65	+ 93 ·46	− 0 ·06
E₃″	33180 ·04	+ 90 ·72	—
E₄	31979 ·95	+ 75 ·65	− 0 ·34
E₄′	31976 ·88	+ 75 ·34	− 0 ·26
E₄″	31931 ·64	+ 78 ·50	− 0 ·20
E₅	30767 ·61	+ 57 ·023	− 0 ·1015
E₅	30766 ·10	+ 57 ·482	− 0 ·191
E₆		Not arranged in series.	

gradually become diffuse, and, at $m = 8$, where the change in the interval is a minimum, they merge to a diffuse patch, apparently terminating the series rather abruptly. After this, there begins a fresh set of lines with an abrupt increase in the interval, which continues regular as far as the lines could be traced; the identification of the last four members is somewhat uncertain owing to the superposition of lines belonging to the band λ 3012·99, which begins here. This new set of lines also begins with characteristic sharpness, but gradually becomes diffuse and separates into two different series with increasing values of m. The first nine lines thus form a series of short range and the rest form two other series, which coalesce at the beginning.

The structure is shown by the curve in fig. 1, which represents the varying distances between successive lines in the three series plotted against successive integral values of m. As may be seen from the curve, none of the series agree throughout their whole length with the linear form implied by the usual formula, but the introduction of a fourth constant with m^3 gives a much
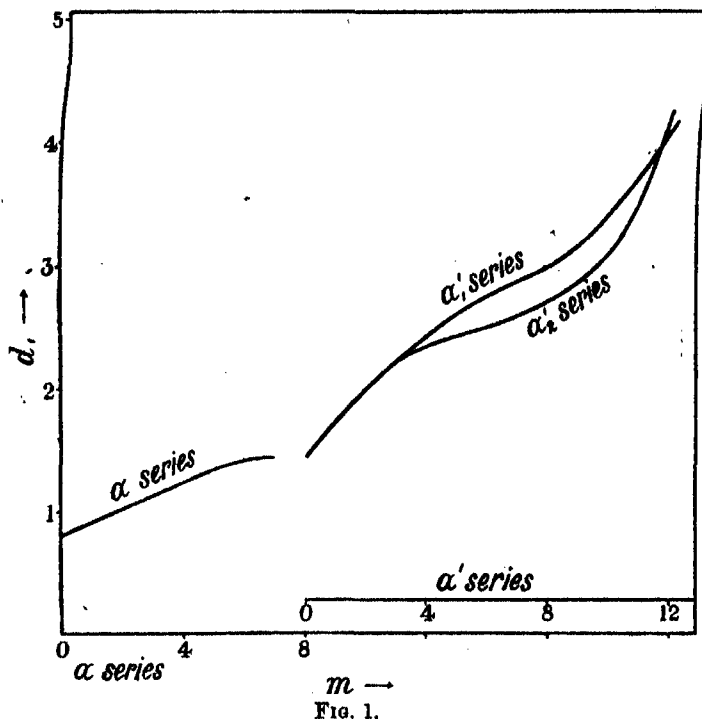
Fig. 1.

closer agreement between the observed and the calculated values. The numerical equations of the various series are :—

Series α ... $\nu = 33214\cdot65 - 0\cdot7259\,m - 0\cdot0525\,m^2 - 0\cdot00015\,m^3$
Series α_1' ... $\nu = 33204\cdot05 - 1\cdot624\,m - 0\cdot125\,m^2 + 0\cdot0022\,m^3$
Series α_2' ... $\nu = 33204\cdot05 - 1\cdot6235\,m - 0\cdot102\,m^2 + 0\cdot0013\,m^3.$

Data for the consideration of regularity in the band are collected in Table III which also shows the differences between the observed and the calculated wave-numbers in the last column. The greatest deviation in wave-number is 0·57, corresponding to a difference of 0·05 A. between the observed and calculated wave-lengths. The error, however, is sufficiently systematic to indicate the imperfection of the formula.

5. *The Relation with the Spectra of other Alkaline Earth Fluorides.*

Each group of BeF_2 bands is composed of alternating double and single heads, and as such the only similarity which they present to the spectra of the other alkaline earth fluorides is with that of the E_1 group of MgF_2. But, while presenting the same appearance, the bands of BeF_2 fade off towards the red, whereas the bands of MgF_2 fade off in the opposite way. For the present,

Table III.—The Series α, α' of the Band λ 3009·85.

α Series.

m.	λ I.A.	ν (vac.).	d_1.	$\nu_{obs.} - \nu_{cal}$.
0	3009 ·85	33214 ·65	0 ·78	0 ·00*
1	09 ·92	213 ·87	0 ·89	0 ·00*
2	10 ·00	212 ·98	0 ·99	0 ·00
3	10 ·09	211 ·99	1 ·10	−0 ·01
4	10 ·18	210 ·89	1 ·22	0 ·00
5	10 ·29	209 ·67	1 ·32	−0 ·02
6	10 ·41	208 ·35	1 ·42	−0 ·01
7	10 ·54	206 ·93	1 ·45	0 ·00*
8	10 ·67	205 ·48		+0 ·08

α_1' Series.

m.	λ I.A.	ν (vac.).	d_1.	$\nu_{obs.} - \nu_{cal}$.
0	3010 ·80	33204 ·05	1 ·75	0 ·00
1	10 ·96	202 ·30	1 ·99	0 ·00
2	11 ·14	200 ·31	2 ·20	0 ·00
3	11 ·34	198 ·11	2 ·43	0 ·00
4	11 ·56	195 ·68	2 ·64	−0 ·01
5	11 ·80	193 ·04	2 ·76	−0 ·04
6	12 ·05	190 ·28	2 ·87	0 ·00
7	12 ·31	187 ·41	2 ·97	+0 ·10
8	12 ·58	184 ·44	3 ·18	+0 ·26
9	12 ·86	181 ·26	3 ·42	+0 ·35
10	13 ·18	177 ·84	3 ·74	+0 ·33
11	13 ·52	174 ·10	4 ·08	+0 ·11
12	13 ·89	170 ·02		−0 ·34

α_2' Series.

m.	λ I.A.	ν (vac.).	d_1.	$\nu_{obs.} - \nu_{cal}$.
0	3010 ·80	33204 ·05	1 ·75	0 ·00
1	10 ·96	202 ·30	1 ·99	−0 ·02
2	11 ·14	200 ·31	2 ·20	−0 ·09
3	11 ·34	198 ·11	2 ·43	−0 ·19
4	11 ·56	195 ·68	2 ·43	−0 ·33
5	11 ·78	193 ·25	2 ·51	−0 ·29
6	12 ·01	190 ·74	2 ·55	−0 ·18
7	12 ·12	188 ·19	2 ·76	+0 ·06
8	12 ·49	185 ·43	2 ·86	+0 ·23
9	12 ·75	182 ·57	3 ·08	+0 ·43
10	13 ·03	179 ·49	3 ·52	+0 ·57
11	13 ·35	175 ·97	4 ·30	+0 ·39
12	13 ·75	171 ·67		−0 ·46

* Used for the calculation of constants.

however, it seems permissible to identify homologous groups by their actual structure, without taking into consideration the direction in which they fade off. This seems to be confirmed by the fact, pointed out in the previous paper, that the value of the constant for class C, calculated from the suggested formula, is very close to that for class A, although these two classes of bands fade off in the opposite direction.

Taking therefore the bands of BeF_2 to be similar to those of the E_1 group of MgF_2, the previous formula

$$\frac{\log b \times \log M}{a} = \text{constant}$$

agrees fairly satisfactorily, as will be seen from Table IV. As before, a and b are constants used for the calculation of series, and M is the molecular number.

Table IV.

Homologous series.	$a = \nu_0$.	b.	M.	$\dfrac{\log b \times \log M}{a}$.
MgF₂ E₁	27149·43	36·475	30	$8\cdot50 \times 10^{-4}$
" E₁'	27145·44	36·435	30	8·50
" E₁''	27123·57	36·7101	30	8·52
BeF₂ E₁	35501·66	129·6	22	7·99
" E₁'	35496·87	129·0	22	7·98
" E₁''	35472·44	127·6	22	7·97
" E₂	34366·73	112·0	22	8·01
" E₂'	34362·25	112·0	22	8·01
" E₂''	34333·00	108·5	22	8·01
" E₃	33217·51	92·326	22	7·94
" E₃'	33214·65	93·46	22	7·96
" E₃''	33180·04	90·72	22	7·92
" E₄	31979·95	75·65	22	7·89
" E₄'	31976·88	75·34	22	7·88
" E₄''	31931·64	78·50	22	7·85

Considering the approximate character of the formula adopted, and the wide range of the values of a, b, and M, the calculated constants agree as closely as could be expected.

Summary.

1. The spectrum of beryllium fluoride, hitherto unrecorded, has been investigated. It has been found to consist of six groups of bands, all in the ultra-violet between $\lambda\,2800$ and $\lambda\,3400$, and all fading off towards the red.

2. The strongest band at $\lambda\,3009$ has been investigated in detail, and has been found to include three series of lines, which depart considerably from the usual type of formula.

3. The groups of bands have been found to be similar to one of the groups of magnesium fluoride, and are related to this group in accordance with the formula for alkaline earth fluorides proposed in a previous paper.

In conclusion, I beg to record my thanks to Prof. A. Fowler, F.R.S., for the kind interest he always takes in my work.

DESCRIPTION OF THE PLATE.

(a) Spectrum of beryllium fluoride between $\lambda\,2820$ and $\lambda\,3140$, showing the groups E_1, E_2, E_3, and a part of E_4.

(b) Spectrum of beryllium fluoride between $\lambda\,3100$ and $\lambda\,3400$, showing the groups E_4 and E_5.

(c) Spectrum of beryllium fluoride, group E_2, showing the structure of the band $\lambda\,3009\cdot85$ with the iron comparison at the top.

(a)

(b)

(c)
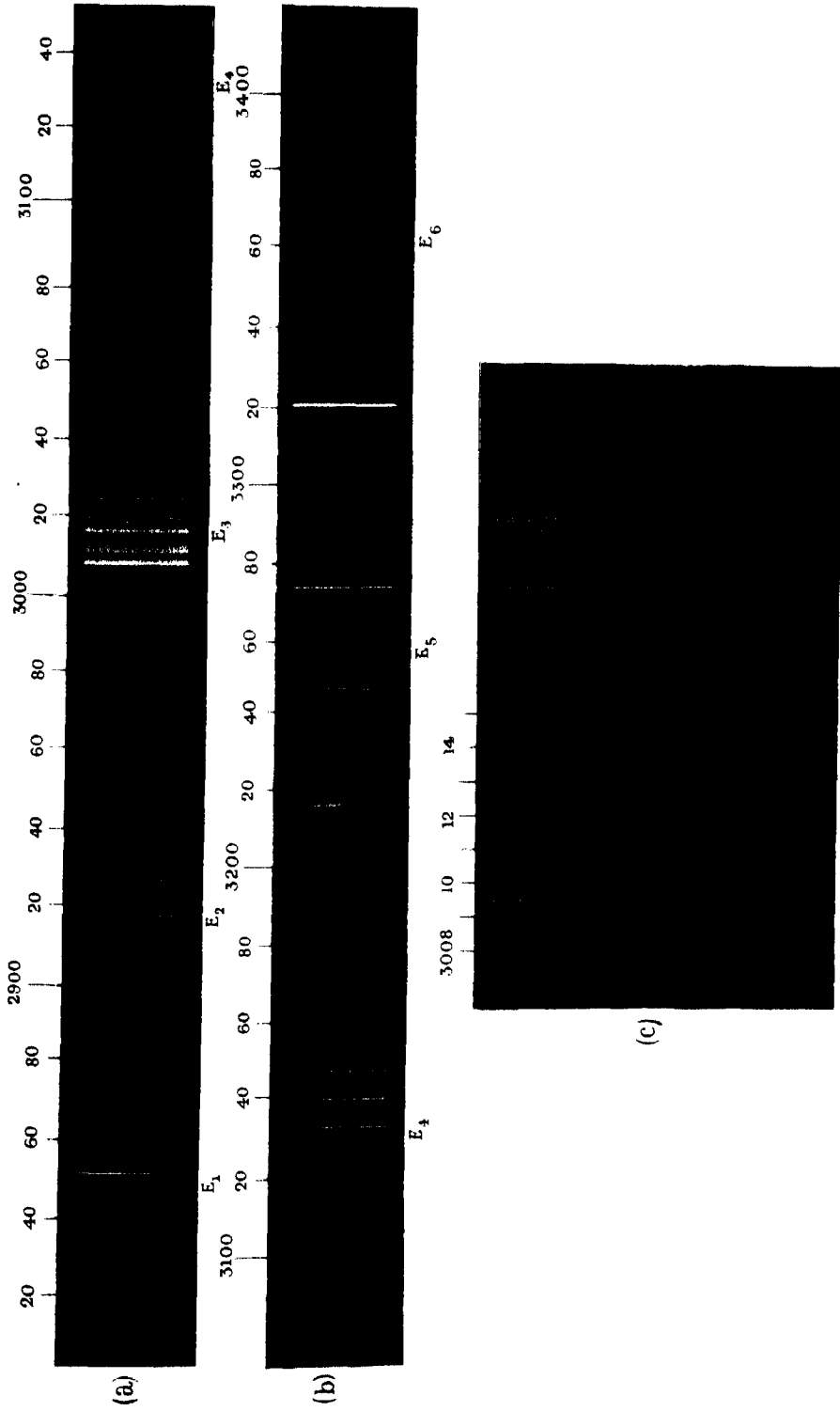
Problems Relating to a Thin Plane Annulus.

By J. W. NICHOLSON, F.R.S., Fellow of Balliol College, Oxford.

CONTENTS.

§ 1. *Introductory.*

The problems which arise in electrostatics and hydrodynamics, in regard to the thin annulus cut from a plane sheet of metal, are of some importance, more especially in regard to electrical instruments of precision, such as the electrometer. Their mathematical solution in an exact form is a matter of extreme difficulty, and only first approximations, which can be derived by simple methods, appear to have been used hitherto. In the present paper, higher approximations are obtained, to an order which appears to be effective for most of the applications which are of real importance. It is shown that the actual difference of radii of the circles bounding the annulus is of comparatively small significance in such magnitudes as the electrical capacity of the annulus, a result which could not readily be foreseen. The whole investigation is only carried to the second order of significance, but by a method—treating the annulus as a special case of the elliptic anchor ring—which can readily be extended to any desired order. The convergence of such approximate solutions is not discussed, but it is clearly analogous to the remarkable degree of convergence found by Lord Rayleigh in certain solutions of problems of vibration of discs in which eccentricity is taken into account.

§ 2. *The Elliptic Anchor Ring, and the Annulus Opening in an Infinite Wall.*

When electricity is freely distributed on a thin plane annulus of inner and outer radii (r_1, r_2), or otherwise, when a thin annulus of this form moves through infinite liquid, or serves as an opening in an infinite plane screen in liquid, we have at present no knowledge of the distribution of electricity, or of fluid motion. In the present paper, by taking such an annulus as a special case of an elliptic anchor ring, some progress is found possible with problems of this nature, though the investigation does not indicate a general exact

Q

solution. From a physical standpoint, however, the solutions obtained would appear to be sufficient.

If co-ordinates (μ, ζ, ω) in space are defined by

$$z = a\mu\zeta, \qquad x = c + a\sqrt{\{(1-\mu^2)(1+\zeta^2)\}}\cos\omega,$$
$$y = c + a\sqrt{\{(1-\mu^2)(1+\zeta^2)\}}\sin\omega,$$

the surfaces $\omega = $ constant are planes $y/x = $ constant, passing through the axis of z.

When ζ is constant, we have

$$\frac{z^2}{a^2\zeta^2} + \frac{(\rho-c)^2}{a^2(1+\zeta^2)} = 1, \qquad \rho = \sqrt{(x^2+y^2)},$$

which is an elliptic anchor ring, the generating ellipses of all such rings being confocal, and the rings becoming, when $c = 0$, oblate spheroids. This system of rings includes, as a special case, the plane annulus

$$z = 0, \qquad \rho = c \pm a,$$

if $c > a$. This corresponds to $\zeta = 0$.

It is seen without difficulty that the surfaces $(\zeta, \mu, \omega) = $ constant are a triply orthogonal system, so that (ζ, μ, ω) may be regarded as orthogonal co-ordinates of any point in space.

We find for the three corresponding space-elements,

$$\delta s_\mu = a\sqrt{\left\{\frac{\mu^2+\zeta^2}{1-\mu^2}\right\}}\,\delta\mu, \qquad \delta s_\zeta = a\sqrt{\left\{\frac{\mu^2+\zeta^2}{\zeta^2+1}\right\}}\cdot\delta\zeta,$$
$$\delta s_\omega = [c + a\sqrt{\{(1-\mu^2)(1+\zeta^2)\}}]\,\delta\omega,$$

resembling the case of oblate spheroidal co-ordinates in space. The internal and external radii of the special annulus are a and c.

We find also for Laplace's equation, when there is symmetry about the axis z

$$\left(\sqrt{(1+\zeta^2)}\frac{\partial}{\partial\zeta}\right)^2\phi + \left(\sqrt{(1-\mu^2)}\frac{\partial}{\partial\mu}\right)^2\phi$$
$$= -\frac{a}{c}\sqrt{(1+\zeta^2, 1-\mu^2)}\left\{\frac{\partial}{\partial\zeta}\left(1+\zeta^2\cdot\frac{\partial\phi}{\partial\zeta}\right) + \frac{\partial}{\partial\mu}\left(1-\mu^2\frac{\partial\phi}{\partial\mu}\right)\right\}$$

which obviously has no exact solutions which are functions of ζ or μ only.

Taking more convenient variables α and β, where

$$\zeta = \sinh\alpha, \qquad \mu = \sin\beta,$$

$$\frac{\partial^2\phi}{\partial\alpha^2} + \frac{\partial^2\phi}{\partial\beta^2} = -\frac{a}{c}\left\{\cos\beta\frac{\partial}{\partial\alpha}\left(\cosh\alpha\frac{\partial\phi}{\partial\alpha}\right) + \cosh\alpha\frac{\partial}{\partial\beta}\left(\cos\beta\frac{\partial\phi}{\partial\beta}\right)\right\}$$

and if a/c is small we may solve this in powers of a/c by successive approximations, the term independent of a/c in any solution being a solution of

$$\frac{\partial^2\phi}{\partial\alpha^2} + \frac{\partial^2\phi}{\partial\beta^2} = 0,$$

$\alpha =$ const. defines the elliptic, and $\beta =$ const. the hyperbolic, anchor rings which belong to the orthogonal system.

On the annulus $z = 0$, ρ ranging from $a - c$ to $a + c$—this is a member of the system—we have $\zeta = 0$, and, therefore, $\alpha = 0$. On the rest of the plane $z = 0$, we have $\mu = 0$, and, therefore, $\beta = 0$. Moreover,

$$\left(\frac{\partial \phi}{\partial \zeta}\right)_{a=0} = \left(\frac{\partial \phi}{\partial \alpha} \cdot \frac{\partial \alpha}{\partial s_\zeta}\right)_{a=0} = \left(\frac{\partial \phi}{\partial \alpha} \cdot \frac{\partial \alpha}{\partial \zeta} \cdot \frac{\partial \zeta}{\partial s_\zeta}\right)_{a=0}$$

$$= \left(\frac{\partial \phi}{\partial \alpha} \cdot \frac{1}{\cosh \alpha} \cdot a^{-1} \sqrt{\frac{\zeta^2 + 1}{\mu^2 + \zeta^2}}\right)_{\substack{a=0 \\ \zeta=0}} = \frac{1}{a\mu}\left(\frac{\partial \phi}{\partial \alpha}\right)_0,$$

$$\left(\frac{\partial \phi}{\partial s_\mu}\right)_{\beta=0} = \left(\frac{\partial \phi}{\partial \beta} \cdot \frac{\partial \beta}{\partial \mu} \cdot \frac{\partial \mu}{\partial s_\mu}\right)_0 = \left[\frac{\partial \phi}{\partial \beta} \cdot \frac{1}{\cos \beta} \cdot \frac{1}{a} \sqrt{\frac{1-\mu^2}{\mu^2+\zeta^2}}\right]_0 = \frac{1}{a\zeta}\left(\frac{\partial \phi}{\partial \beta}\right)_0,$$

and when $\zeta = 0$, on the annulus,

$$\rho - c = a\sqrt{(1-\mu^2)},$$

or $\qquad \mu = \sqrt{\left\{1 - \frac{(\rho-c)^2}{a^2}\right\}}, \qquad a\mu = \sqrt{\{(\overline{a+c}-\rho)(\overline{a-c}+\rho)\}}$

making β and μ vanish at each edge.

On the rest of the plane, when $\mu = 0$,

$$a^2(1+\zeta^2) = (\rho-c)^2, \qquad \zeta = \sqrt{\left\{\frac{(\rho-c)^2}{a^2}-1\right\}}, \qquad a\zeta = \sqrt{(\rho-\overline{c+a} \cdot \rho-\overline{c-a})},$$

so that ζ and α also vanish at each edge.

When a is sufficiently small in comparison with c, the solutions approximate to those of

$$\frac{\partial^2 \phi}{\partial \alpha^2} + \frac{\partial^2 \phi}{\partial \beta^2} = 0,$$

of which the only solutions not dependent on β are

$$\phi = A + B\alpha.$$

Consider the solution $\phi = \alpha$. This makes ϕ zero when $\alpha = 0$, and when $\beta = 0$, on the plane $z = 0$,

$$\frac{\partial \phi}{\partial n} = \frac{1}{a\zeta}\frac{\partial \phi}{\partial \beta} = 0.$$

It is thus apparently suitable for the motion of a liquid through a thin annular opening in the barrier $z = 0$, satisfying all the conditions approximately. These are (1) the differential equation; (2) ϕ constant when $\alpha = 0$; (3) $\partial \phi/\partial n = 0$ when $\beta = 0$; (4) ϕ continuous at the edges where $\alpha = 0$.

We find also on the aperture,

$$\frac{\partial \phi}{\partial n} = \frac{1}{a\mu}\left(\frac{\partial \phi}{\partial \alpha}\right)_0 = \frac{1}{a\mu} = \frac{1}{\sqrt{\{(a+c-\rho)(a-c+\rho)\}}}.$$

The velocity is infinite to order $\frac{1}{2}$ at both edges. This is to be expected,

and might in fact have been written down at once as the necessary approximate solution, from our knowledge of the effect at the edge in the case of a circular aperture, or a stream flowing past a circular obstacle. We must now proceed by successive approximations to a solution of the form

$$\phi = \alpha + \frac{a}{c} f_1 + \left(\frac{a^2}{c^2}\right) f_2 + \left(\frac{a^3}{c^3}\right) f_3 + \dots$$

where the functions f_n must possess the following properties:—

(1) ϕ is a solution of the differential equation, to some specified order of a/c.

(2) $f_n = 0$ when $\alpha = 0$.

(3) $\partial f_n/\partial \beta = 0$ when $\beta = 0$.

The second secures that $\phi = 0$ over the aperture, and the third that $\partial \phi/\partial z = 0$ over the rest of the plane $z = 0$. The third is satisfied necessarily if f_n contains only cosines of β and its multiples as multipliers of its terms in α. It is, of course, understood that the series may cease to be applicable when α is large, and require another form of continuation.

Writing $\phi = \alpha + \frac{a}{c} \psi_1$ in the differential equation, we find, neglecting terms of order $(a/c)^2$,

$$\frac{\partial^2 \psi_1}{\partial \alpha^2} + \frac{\partial^2 \psi_1}{\partial \beta^2} = -\left\{ \cos\beta \frac{\partial}{\partial\alpha} \cosh\alpha \frac{\partial}{\partial\alpha} + \cosh\alpha \frac{\partial}{\partial\beta} \cos\beta \frac{\partial\alpha}{\partial\beta} \right\} = -\cos\beta \sinh\alpha,$$

of which the particular integral is

$$\psi_1 = -\tfrac{1}{2} \alpha \cosh\alpha \cos\beta.$$

No complementary function satisfying

$$\frac{\partial^2 \psi_1}{\partial\alpha^2} + \frac{\partial^2 \psi_1}{\partial\beta^2} = 0$$

must be added, for it would represent *another* approximate solution of the original equation, multiplied by c/a, in its first term. We must, in fact, throughout the work, notice that no term appears which is itself a solution of this equation, but this will not occur if the particular integrals are obtained according to the ordinary rules in linear differential equations.

The second approximation to ϕ is therefore

$$\phi = \alpha - \frac{\alpha}{2} \frac{a}{c} \cosh\alpha \cos\beta$$

where $f_1 = -\tfrac{1}{2} \alpha \cosh\alpha \cos\beta$

with the necessary properties, as a function of α or of β.

Now write

$$\phi = \alpha - \frac{\alpha a}{2c}\cosh\alpha\cos\beta + \frac{a^2}{c^2}\psi_2$$

and neglecting a^3/c^3, we have

$$\frac{\partial^2\psi_2}{\partial\alpha^2} + \frac{\partial^2\psi_2}{\partial\beta^2} = + \left(\cos\beta\frac{\partial}{\partial\alpha}\cosh\alpha\frac{\partial}{\partial\alpha} + \cosh\alpha\frac{\partial}{\partial\beta}\cos\beta\frac{\partial}{\partial\beta}\right)\frac{\alpha}{2}\cosh\alpha\cos\beta$$

$$= \tfrac{1}{8}(3\sinh 2\alpha + 2\alpha\cosh 2\alpha) + \tfrac{1}{8}\cos 2\beta(3\sinh 2\alpha - 2\alpha),$$

and on solution

$$\psi_2 = \tfrac{1}{32}(\sinh 2\alpha + 2\alpha\cosh 2\alpha) + \tfrac{1}{32}\cos 2\beta(2\alpha + 3\alpha\cosh 2\alpha).$$

This also has the properties $(\psi_2)_{\alpha=0} = 0$, $(\partial\psi_2/\partial\beta)_{\beta=0} = 0$.

The third approximation to ϕ is now known. If ψ_3 is the next function required,

$$\frac{\partial^2\psi_3}{\partial\alpha^2} + \frac{\partial^2\psi_3}{\partial\beta^2} = -\left\{\cos\beta\frac{\partial}{\partial\alpha}\cosh\alpha\frac{\partial}{\partial\alpha} + \cosh\alpha\frac{\partial}{\partial\beta}\cos\beta\frac{\partial}{\partial\beta}\right\}\psi_2,$$

from which ψ_3 is of the form $P\cos\beta + Q\cos 3\beta$, where P and Q are functions of α vanishing when α is zero. The comparative simplicity of the coefficients in these functions does not, however, continue, although it is quite easy to continue the approximation to a high order. It has already gone far enough for most purposes, on account of the great initial convergency of the series over the aperture. We may, therefore, write, to order a^3/c^2,

$$\phi = \alpha - \frac{\alpha a}{2c}\cosh\alpha\cos\beta + \frac{a^2}{32c^2}(\sinh 2\alpha + 2\alpha\cosh 2\alpha)$$

$$+ \frac{a^2\cos 2\beta}{32c^2}(2\alpha + 3\alpha\cosh 2\alpha).$$

The normal velocity over the aperture is therefore

$$\frac{1}{a\mu}\left(\frac{\partial\phi}{\partial\alpha}\right)_{\alpha=0} = \frac{1}{a\mu}\left\{1 - \frac{a}{2c}\cos\beta + \frac{a^2}{8c^2} + \frac{5}{32}\frac{a^2}{c^2}\cos 2\beta\right\}$$

where

$$(\rho - c)/a = \sqrt{(1-\mu^2)} = \cos\beta,$$

and the velocity thus becomes

$$(c+a-\rho)^{-\frac{1}{2}}(\rho-c+a)^{-\frac{1}{2}}\left\{1 - \frac{a^2}{32c^2} - \frac{\rho-c}{2c} + \frac{5}{16}\frac{(\rho-c)^2}{c^2}\right\}$$

the value at the centre being

$$\frac{1}{a}\left(1 - \frac{a^2}{32c^2}\right).$$

For a velocity U at the central radius $\rho = c$, the velocity U_ρ at ρ is

$$U_\rho = \frac{aU}{\sqrt{\{(c+a-\rho)(\rho-c+a)\}}}\left\{1 - \frac{\rho-c}{2c} + \frac{5}{16}\frac{(\rho-c)^2}{c^2}\right\}.$$

The volume V discharged through the aperture in unit time is

$$V = \int_{c-a}^{c+a} 2\pi\rho\, U_\rho d\rho = 4\pi a U \int_0^{\pi/2} d\phi \left\{ \rho - \frac{\rho\,(\rho-c)}{2c} + \frac{5}{16}\,\frac{\rho\,(\rho-c)^2}{c^2} \right\}$$

(with $\rho = \overline{c-a} \cdot \cos^2\phi + \overline{c+a} \cdot \sin^2\phi$),

and after an easy integration,

$$V = 2\pi^2 ac\, U \left(1 - \frac{3a^2}{32c^2} \right)$$

no term appearing on a/c. The average velocity over the area is

$$\frac{\pi}{2}\, U \left(1 - \frac{3a^2}{32c^2} \right)$$

where U is the velocity at the central radius.

The stream surfaces are almost identical with the hyperbolic anchor rings

$$\frac{(\rho-c)^2}{a^2(1-\mu^2)} - \frac{z^2}{a^2\mu^2} = 1$$

where μ is constant.

It is evident that the formulæ, even to this approximation, may be used with accuracy of a few per cent. even in such a case as $a = \frac{1}{2}c$.

The Bessel-Fourier solution to this order is, in the plane of the annulus,

$$\left(\frac{\partial\phi}{\partial z}\right)_{z=0} = \int_0^\infty \lambda J_0(\lambda\rho)\, d\lambda \int_{c-a}^{c+a} \mu J_0(\lambda\mu)\, U_\mu\, d\mu$$

so that more generally

$$\phi = -\int_0^\infty J_0(\lambda\rho)\, e^{-\lambda z}\, d\lambda \int_{c-a}^{c+a} \mu\, J_0(\lambda\mu)\, U_\mu\, d\mu$$

and on the axis of z, where $\rho = 0$,

$$\phi = -\int_{c-a}^{c+a} \mu\, U_\mu\, \frac{d\mu}{\sqrt{(z^2+\mu^2)}}.$$

If z is less than $c-a$, we can obtain a convergent series in powers of z, of the form

$$\phi = -\sum_0^\infty (-)^n\, \frac{2n\,!}{2^{2n}\,(n\,!)^2} \cdot z^{2n} \int_{c-a}^{c+a} \frac{d\mu\, U_\mu}{\mu^{2n}}$$

and its appropriate generalisation, in the usual way, as a series of zonal harmonics, valid when $r < c-a$,

$$\phi = -Ua \sum_0^\infty (-)^n\, \frac{2n\,!}{2^{2n}\,(n\,!)^2}\, r^{2n}\, P_{2n}(\mu) \int_{c-a}^{c+a} \frac{d\mu\,\{1 - (\mu-c)/2c + 5\,(\mu-c)^2/16c^2\}}{\mu^{2n}\,\sqrt{\{(c+a-\mu)(\mu-c+a)\}}}.$$

The corresponding harmonic series for a distant point can obviously be written down in a similar manner.

As a special case, the value of ϕ over the plane $z = 0$, for points at which $\rho < c - a$, on part of the barrier, is

$$\phi = -\sum_{0}^{\infty} \left[(-)^n \frac{2n!}{2^{2n} (n!)^2} \right]^2 \rho^{2n} \int_{c-a}^{c+a} \frac{d\mu}{\mu^{2n}} U_\mu$$

$$= -Ua \int_{c-a}^{c+a} K\left(\frac{\rho}{\mu}\right) \frac{d\mu}{\sqrt{\{(c+a-\mu)(\mu-c+a)\}}} \left\{ 1 - \frac{\mu-c}{2c} + \frac{5}{16} \frac{(\mu-c)^2}{c^2} \right\}$$

where $K(\rho/\mu)$ is the complete elliptic integral of modulus ρ/μ. Since ρ and μ are nearly equal, this can be evaluated approximately by use of the logarithmic form of K.

§ 3. *The Electrified Thin Annulus. Surface Density and Charge.*

The last problem is analytically identical with that of the distribution of free electricity on a thin annular conductor, and we can replace normal velocity over the aperture by surface density over the annular conductor. For V, the electric potential, is constant over the conductor, and $\partial V/\partial z = 0$ over the rest of its plane. If c/a is very large—the radii being $c-a$, $c+a$—the potential at a point close to the conductor is evidently that produced by an indefinitely long thin plate of breadth $2a$, which is a special case of the elliptic cylinder, when the minor axis of the principal elliptic section degenerates to zero. If the same axes of this section were, in the first place, $a\zeta_0$, $a\sqrt{(1+\zeta_0^2)}$, the potential at an external point (z, ρ) would be, as regards its variable part, proportional to

$$\int_\lambda \frac{dt}{\sqrt{\{(a^2\zeta_0^2 + t)\}\{(a^2(1+\zeta_0^2)+t)\}}}.$$

Writing

$$t = a^2\zeta_0^2 \sinh^2 u - a^2 (1 + \zeta_0^2) \cosh^2 u,$$

the integral becomes

$$2 \int_\lambda du = (2u)_{t=\lambda} + \text{const.}$$

Now λ is the parameter of the ellipse through (z, ρ) defined by

$$\frac{z^2}{a^2\zeta_0^2 + \lambda} + \frac{\rho^2}{a^2 + a^2\zeta_0^2 + \lambda} = 1.$$

With the spheroidal co-ordinates $z = a\mu\zeta$, $\rho = a \sqrt{(1-\mu^2 \cdot 1 + \zeta^2)}$ we find $\lambda = a^2(\zeta^2 - \zeta_0^2)$, so that $(u)_{t=\lambda}$ is given by

$$a^2\zeta_0^2 \sinh^2 u - a^2 (1 + \zeta_0^2) \cosh^2 u = \lambda = a^2 (\zeta^2 - \zeta_0^2),$$

or
$$(u)_{t=\lambda} = \sinh^{-1} \zeta = \alpha,$$

where α is the variable occurring in the previous section.

Thus, when c/a is large, the potential of the elliptic anchor ring of oblate type is of the form $A + B\alpha$ at external points just outside, if it is very flat.

This justifies our selection of α as the solution from which a further

approximation was to be obtained, and rules out other functions, which at first sight might appear suitable.

The surface density of a free distribution on a thin annulus of radii $c \pm a$ is therefore proportional to the value of $\partial \phi / \partial n$ in the last section, or

$$\sigma = \frac{\sigma_0 a}{\sqrt{\{(c+a-\rho)(\rho-c+a)\}}} \left\{ 1 - \frac{\rho-c}{2c} + \frac{5}{16} \frac{(\rho-c)^2}{c^2} \right\}$$

and the total charge Q on one side becomes on integration

$$\bullet \quad Q = 2\pi^2 a c \sigma_0 \left(1 - \frac{3a^2}{32c^2} \right),$$

σ_0 being the density at the central circle.

In order to find the capacity of the annulus, we require the potential produced by this distribution at a point of the annulus. Hitherto, it has been an additive constant of unknown magnitude in the investigation. We find it by direct integration for a point $\rho = c+a$ on the outer edge, for it is the same at all points on the annulus.

4. *Capacity of a Thin Annulus.*

The potential of a circular ring of charge E at a point distant f from its centre,—f not less than the radius,—in its plane is

$$V = \frac{E}{\pi} \int_0^\pi \frac{d\theta}{\sqrt{(\rho^2+f^2-2f\rho \cos \theta)}}$$

where ρ is the radius of the ring. This becomes, if K is the complete elliptic function,

$$V = \frac{2E}{\pi} \cdot \frac{1}{\rho+f} K\left(\frac{2\sqrt{(\rho f)}}{\rho+f} \right).$$

Let $f = c+a$, and let ρ be approximately equal to f. The modulus k of the elliptic function is $2 \sqrt{(\rho f)}/(\rho+f)$, so that, in the usual notation, $k' = (f-\rho)/(f+\rho)$ and is nearly zero. Thus, in fact, on expansion in powers of a/c or $(\rho-f)/c$,

$$k' = \frac{a+c-\rho}{a+c+\rho} = \frac{a+c-\rho}{2c+(a+\rho-c)}$$

$$= \frac{a+c-\rho}{2c} \left\{ 1 - \frac{a+\rho-c}{2c} + \frac{(a+\rho-c)^2}{4c^2} \right\}$$

to a sufficient order. Moreover*

$$K(k) = \left(1 + \tfrac{1}{4}k'^2 + \frac{9}{64} k'^4 \right) \log_e \left(\frac{4}{k'} \right) - 2 \left(\frac{1}{1.2} \right) \tfrac{1}{4}k'^2 - 2 \left(\frac{1}{1.2} + \frac{1}{3.4} \right) \frac{9}{64} k'^4$$

where the approximation

$$K(k) = (1 + \tfrac{1}{4}k'^2) \log_e \left(\frac{4}{k'} \right) - \tfrac{1}{4}k'^2$$

* Cayley, 'Elliptic Functions,' p. 541.

is all that we require, to relative order a^2/c^2. Thus

$$K(k) = -\left\{1 + \frac{(a+c-\rho)^2}{16c^2}\right\}\log\left(\frac{a+c-\rho}{8c}\right)$$

$$+ \frac{a+\rho-c}{2c}\left(1 - \frac{a+\rho-c}{4c}\right)\left(1 + \frac{(a+c-\rho)^2}{16c^2}\right)\frac{(a+c-\rho)^2}{16c^2}$$

$$= -\left(1 + \frac{(a+c-\rho)^2}{16c^2}\right)\log\left(\frac{a+c-\rho}{8c}\right)$$

$$+ \frac{a+\rho-c}{2c} - \frac{3a^2 + 3(\rho-c)^2 + 2a(\rho-c)}{16c^2},$$

also

$$\frac{1}{\rho+f} = \frac{1}{\rho+a+c} = \frac{1}{2c}\left\{1 - \frac{a+\rho-c}{2c} + \frac{(a+\rho-c)^2}{4c^2}\right\},$$

and we find ultimately

$$\frac{2c\pi V}{2E} = -\left(1 - \frac{a+\rho-c}{2c} + \frac{4(a+\rho-c)^2 + (a+c-\rho)^2}{16c^2}\right)\log_e\left(\frac{a+c-\rho}{8c}\right)$$

$$+ \frac{a+\rho-c}{2c} - \frac{7a^2 + 7(\rho-c)^2 + 10a(\rho-c)}{16c^2}$$

Writing now, $E = 2\pi\rho\,d\rho\,.\,\sigma$, where σ is the surface density of the last section, the potential of the annulus is obtained in the form

$$V_0 = \frac{2}{c}\int_{c-a}^{c+a}\rho\sigma\,d\rho\,.\,f(\rho)$$

where $f(\rho)$ is the function of ρ on the right of the previous equation, and

$$\sigma = \frac{\sigma_0 a}{\sqrt{\{(c+a-\rho)(\rho-c+a)\}}}\left\{1 - \frac{\rho-c}{2c} + \frac{5}{16}\frac{(\rho-c)^2}{c^2}\right\}.$$

The integration is very tedious. With $\rho = (c-a)\cos^2\theta + (c+a)\sin^2\theta$, we find

$$V_0 = \frac{4\theta\sigma_0}{c}\int_0^{\pi/2}\rho\,d\theta\,.\,F(\rho)$$

where

$$F(\rho) = F_1(\rho) + F_2(\rho),$$

$$F_1(\rho) = -\left\{1 - \frac{a+2\rho-2c}{2c} + \frac{5a^2 + 14(\rho-c)^2 + 10a(\rho-c)}{16c^2}\right\}\log\left(\frac{a+c-\rho}{8c}\right).$$

$$F_2(\rho) = \frac{a+\rho-c}{2c} - \frac{7a^2 + 11(\rho-c)^2 + 14a(\rho-c)}{16c^2}.$$

If

$$cV_0 = 4a\sigma_0(V_0^1 + V_0^2)$$

where V_0^1, V_0^2 are the portions of the integral arising from $F_1(\rho)$, $F_2(\rho)$, we easily find

$$V_0^2 = \frac{\pi a(a+2c)}{8c} \quad \frac{7\pi a^2}{32c} - \frac{11\pi a^2}{64c} - \frac{7\pi a^3}{32c^2} = \frac{\pi a}{4}\left(1 - \frac{17a}{16c}\right)$$

to the present order. Moreover

$$\log\left(\frac{a+c-\rho}{8c}\right) = \log\frac{a}{4c} + 2\log\cos\theta$$

and $V_0{}^1 = -\log\dfrac{a}{4c}\displaystyle\int_0^{\pi/2}\rho\,d\theta\left\{1 - \frac{a+2\rho-2e}{2c} + \frac{5a^2+14(\rho-c)^2+10a(\rho-c)}{16c^2}\right\}$

$$-2\int_0^{\pi/2}\left(1 - \frac{a}{2c} + \frac{5a^2}{16c^2}\right)\log\cos\theta\,d\theta\,\{(c-a)\cos^2\theta + (c+a)\sin^2\theta\}$$

$$+\frac{4a}{2c}\left(1 - \frac{5a}{8c}\right)\int_0^{\pi/2}[(c-a)\cos^2\theta + (c+a)\sin^2\theta]$$

$$\log\cos\theta\,d\theta\,(2\sin^2\theta - 1)$$

$$-\frac{7a^2}{4c^2}\int_0^{\pi/2}[(c-a)\cos^2\theta + (c+a)\sin^2\theta]\log\cos\theta\,d\theta\,(2\sin^2\theta - 1)^2.$$

These integrals can all be evaluated. If they are called I_1, I_2, I_3, I_4, then

$$V_0{}^1 = \log\frac{4c}{a}\,.\,I_1 - 2I_2 + \frac{2a}{c}\left(1 - \frac{5a}{8c}\right)I_3 - \frac{7a^2}{4c^2}\,I_4\,.$$

We find

$$I_1 = \frac{\pi c}{2}\left(1 - \frac{a}{2c} + \frac{5a^2}{16c^2}\right) - \frac{\pi a^2}{4c}\left(1 - \frac{5a}{8c}\right) + \frac{7\pi a^2}{32c}$$

$$= \frac{\pi c}{2}\left(1 - \frac{a}{2c} + \frac{a^2}{4c^2}\right)$$

to the requisite order.

It is well known, and easily proved, that

$$\int_0^{\pi/2}\log\cos\theta\,d\theta = -\frac{\pi}{2}\log 2.$$

By an easy integration by parts, we find also

$$2n\int_0^{\pi/2}\sin^{2n}\theta\log\cos\theta\,d\theta = (2n-1)\int_0^{\pi/2}\sin^{2n-2}\theta\log\cos\theta\,d\theta - \int_0^{\pi/2}\sin^{2n}\theta\,d\theta,$$

so that

$$\int_0^{\pi/2}\sin^2\theta\log\cos\theta\,d\theta = -\frac{\pi}{4}\log 2 - \frac{\pi}{4},$$

$$\int_0^{\pi/2}\sin^4\theta\log\cos\theta\,d\theta = -\frac{3\pi}{16}\log 2 - \frac{15\pi}{64},$$

$$\int_0^{\pi/2}\sin^6\theta\log\cos\theta\,d\theta = -\frac{5\pi}{32}\log 2 - \frac{85\pi}{384}.$$

Thus

$$I_2 = \left(1 - \frac{a}{c} + \frac{5a^2}{16c^2}\right)\int_0^{\pi/2}\{(c-a) + 2a\sin^2\theta\}\log\cos\theta\,d\theta$$

$$= c\left(1 - \frac{a}{c} + \frac{5a^2}{16c^2}\right)\left(-\frac{\pi}{2}\log 2\right) - \frac{\pi a}{2}\left(1 - \frac{a}{c} + \frac{5a^2}{16c^2}\right)$$

$$= -\frac{\pi c}{2}\log 2\left(1 - \frac{a}{c} + \frac{5a^2}{16c^2}\right) - \frac{\pi c}{2}\,.\,\frac{a}{c}\left(1 - \frac{a}{c}\right)$$

to the proper order,

$$I_3 = \int_0^{\pi/2} \{-(c-a)+(2c-4a)\sin^2\theta + 4a\sin^4\theta\}\log\cos\theta\,d\theta$$

$$= \frac{\pi}{2}\log 2 \cdot (c-a)-(2c-4a)\left(\frac{\pi}{4}\log 2 + \frac{\pi}{4}\right)-4a\left(\frac{3\pi}{16}\log 2 + \frac{15\pi}{64}\right)$$

$$= -\frac{\pi c}{4}\log 2 \cdot \left(\frac{a}{c}\right)-\frac{\pi c}{2}\left(1-\frac{a}{8c}\right),$$

$$I_4 = \int_0^{\pi/2} [c-a+(6a-4c)\sin^2\theta + (4c-12a)\sin^4\theta + 8a\sin^6\theta]\log\cos\theta\,d\theta$$

$$= -\frac{\pi}{2}\log 2\,(c-a)+(4c-6a)\left(\frac{\pi}{4}\log 2 + \frac{\pi}{4}\right)$$

$$\qquad\qquad +(12a-4c)\left(\frac{3\pi}{16}\log 2 + \frac{15\pi}{64}\right)-8a\left(\frac{5\pi}{32}\log 2 + \frac{85\pi}{384}\right)$$

$$= -\frac{\pi c}{4}\log 2 + \frac{\pi c}{16}\left(1-\frac{22a}{3c}\right),$$

and accordingly

$$V_0{}^1 = \log\frac{4c}{a} \cdot I_1-2I_2+\frac{2a}{c}\left(1-\frac{5a}{8c}\right)I_3-\frac{7a^2}{4c^2}I_4$$

$$= \frac{\pi c}{2}\left(1-\frac{a}{2c}+\frac{a^2}{4c^2}\right)\log\frac{4c}{a} + \pi c \cdot \frac{a}{c}\left(1-\frac{a}{c}\right)+\frac{2a^2}{c^2}\left(-\frac{\pi c}{4}\log 2\right)$$

$$-\pi c \cdot \frac{a}{c}\left(1-\frac{5a}{8c}\right)\left(1-\frac{a}{8c}\right)+\frac{7\pi c}{16}\frac{a^2}{c^2}\log 2 -\frac{7}{64}\pi c \cdot \frac{a^2}{c^2}$$

$$= \frac{\pi c}{2}\left(1-\frac{a}{2c}+\frac{a^2}{4c^2}\right)\log\frac{4c}{a} + \pi c \log 2\left(1-\frac{a}{c}+\frac{a^2}{4c^2}\right)-\frac{23}{64}\pi c \cdot \frac{a^2}{c^2}$$

$$= \frac{\pi c}{2}\left(1-\frac{a}{2c}+\frac{a^2}{4c^2}\right)\log\frac{16c}{a} -\pi c \cdot \frac{a^2}{c^2} \cdot \frac{23}{64},$$

the terms involving the logarithms condensing elegantly.

The whole potential of the annulus is finally

$$V_0 = \frac{4a\sigma_0}{c}(V_0{}^1+V_0{}^2)$$

$$= \frac{4a\sigma_0}{c} \cdot \frac{\pi c}{2}\left(1-\frac{a}{2c}+\frac{a^2}{4c^2}\right)\log\frac{16c}{a} + \frac{4a\sigma_0}{c}\left\{\frac{\pi c}{4} \cdot \frac{a}{c}-\pi c\left(\frac{17}{64}\frac{a^2}{c^2}+\frac{23}{64}\frac{a^2}{c^2}\right)\right\}$$

$$= 2\pi a\sigma_0\left\{\left(1-\frac{a}{2c}+\frac{a^2}{4c^2}\right)\log\frac{16c}{a} + \frac{a}{2c}\left(1-\frac{5a}{2c}\right)\right\}$$

where σ_0 is the central density.

The total charge on one side was

$$Q = 2\pi^2 ac\sigma_0\left(1-\frac{3a^2}{32c^2}\right)$$

and the complete charge being twice this amount, the capacity of the annulus is

$$2\pi c\left(1-\frac{3a^2}{32c^2}\right) \Big/ \left\{\left(1-\frac{a}{2c}+\frac{a^2}{4c^2}\right)\log\frac{16c}{a}+\frac{a}{2c}\left(1-\frac{5a}{2c}\right)\right\}$$

which can be used with some accuracy if a is less than about $\frac{1}{4}c$. A higher approximation could be worked out readily by this analysis.

Numerical calculations give results agreeing in general terms with those corresponding to the ordinary anchor ring of radii (a, c), for which the capacity is already known.*

The error in this formula is roughly of order $(a/c)^3$, or only 1 or 2 per cent. if $a=\frac{1}{4}c$. If a is so small as $\frac{1}{10}c$, we may drop the terms in $(a/c)^2$, and use the simpler form

$$2\pi c\left\{1+\frac{a}{2c}\left(\log_e\frac{16c}{a}-1\right)\right\}.$$

In the Table typical values are given. The radii are $c\pm a$, so that c is the mean radius of the annulus:—

a/c.	(Capacity)/$2\pi c$.
0·05	0·177
0·1	0·205
0·15	0·227
0·2	0·247
0·25	0·263
0·3	0·283

The presence of an inner edge much increases the capacity, as the laws of electrical distribution require that the surface density becomes large there. A complete circular disc of radius $2c$, and therefore of mean radius c, has a capacity

$$4c/\pi \quad\text{or}\quad 2\pi c\times\frac{2}{\pi^2} = 2\pi c\times 0\cdot20264.$$

Thus, an annulus of the same *mean* radius, and $a/c = 1/10$, has practically the same capacity. There will be another annulus which has a *maximum* capacity for a given mean radius, but the present approximation does not allow us to determine it precisely. It is clearly one with a very small opening at the centre.

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* Hicks, 'Phil. Trans.,' and Dyson, 'Phil. Trans.,' 1893.

§ 5. *Axial Motion of an Annulus through Infinite Liquid.*

When an ellipsoid of semi-axes (a, b, c) moves parallel to the axis x, corresponding to a, it creates a velocity potential at (x, y, z) equal to

$$\phi = \frac{abc\,U}{2-\alpha_0} \cdot x \int_\lambda^\infty \frac{dt}{(a^2+t)^{3/2}(b^2+t)^{1/2}(c^2+t)^{1/2}}$$

where

$$\alpha_0 = abc \int_0^\infty \frac{dt}{(a^2+t)^{3/2}(b^2+t)^{1/2}(c^2+t)^{1/2}}$$

U is the velocity of the ellipsoid, and λ is the parameter of the confocal through (x, y, z). For the special case of an elliptic cylinder, $c = \infty$, and we find

$$\alpha_0 = ab \int_0^\infty \frac{dt}{(a^2+t)^{3/2}(b^2+t)^{1/2}} = -\frac{2}{b^2-a^2}\left(\coth u\right)_{t=0}^{t=\infty}$$

where

$$t = -a^2\cosh^2 u + b^2\sinh^2 u,$$

or

$$\alpha_0 = -\frac{2ab}{b^2-a^2}\left(\coth u\right)_{u=\coth^{-1}b/c}^{u=\infty} = -\frac{2}{b^2-a^2}\left(\frac{b}{a}-1\right) = -\frac{2b}{(a+b)}.$$

We have assumed that b is the semi-axis *major*, so that it moves along the minor axis. The value of ϕ for the elliptic cylinder becomes

$$\phi = \frac{bUx}{b-a}(\coth^{-1}u-1) \text{ with } \lambda = -a^2\cosh^2 u + b^2\sinh^2 u,$$

or

$$\phi = \frac{bUx}{b-a}\left\{\sqrt{\left(\frac{b^2+\lambda}{a^2+\lambda}\right)}-1\right\}.$$

This result is not usually given in the text-books, although very convenient. If we use instead the co-ordinates (μ, ζ) defined by

$$x = a\mu\zeta, \qquad y = a\sqrt{(1-\mu^2 \cdot 1 + \zeta^2)}$$

and define the moving cylinder by $\zeta = \zeta_0$, the equation of the cylinder is

$$\frac{x^2}{a^2\zeta_0^2} + \frac{y^2}{a^2(1+\zeta_0^2)} = 1,$$

and the parameter λ of an external point is

$$\lambda = a^2(\zeta^2 - \zeta_0^2)$$

while a^2 is replaced by $a^2\zeta_0^2$, and b^2 by $a^2(1+\zeta_0^2)$, so that

$$\phi = \frac{aU\mu}{1-\zeta_0/\sqrt{(1+\zeta_0^2)}}\{\sqrt{(1+\zeta^2)}-\zeta\}.$$

This is the velocity potential created by the motion of the cylinder ζ_0 of the family

$$\frac{x^2}{a^2\zeta^2} + \frac{y^2}{a^2(1+\zeta^2)} = 1$$

parallel to the axis of x. With co-ordinates $\alpha = \sinh^{-1} \zeta$, $\beta = \sin^{-1} \mu$, the elliptic cylinder

$$\frac{x^2}{a^2 \sinh^2 \alpha_0} + \frac{y^2}{a^2 \cosh^2 \alpha_0} = 1$$

creates, in motion parallel to x, the potential

$$\phi = \frac{aU \sin \beta (\cosh \alpha - \sinh \alpha)}{1 - \tanh \alpha_0}$$

which is, of course, readily deducible also from the two-dimensional solution.

The elliptic anchor ring, the minor axis of whose section is parallel to the axis of the ring, produces, in motion along the axis of the ring, a velocity potential ϕ close to its surface, to which this formula gives a first approximation. The co-ordinates $(\alpha \beta)$ are those already used in this paper, and the present mode of approach indicates their relation to the usual "elliptic co-ordinates" of two dimensions.

Thus for motion of an elliptic anchor ring of the type in question,

$$\phi = \sin \beta e^{-\alpha}$$

is the solution of

$$\frac{\partial^2 \phi}{\partial \alpha^2} + \frac{\partial^2 \phi}{\partial \beta^2} = 0$$

to which the true velocity potential, satisfying

$$\frac{\partial^2 \phi}{\partial \alpha^2} + \frac{\partial^2 \phi}{\partial \beta^2} = -\frac{a}{c} \left\{ \cos \beta \frac{\partial}{\partial \alpha} \cosh \alpha \frac{\partial \phi}{\partial \alpha} + \cosh \alpha \frac{\partial}{\partial \beta} \cos \beta \frac{\partial \phi}{\partial \beta} \right\},$$

approximates when a/c tends to zero.

Write therefore, for the anchor ring, or for the circular annulus $\alpha_0 = 0$ which we shall alone consider.

$$\phi = e^{-\alpha} \sin \beta + \frac{a}{c} \psi_1 + \frac{a^2}{c^2} \psi_2 + \frac{a^3}{c^3} \psi_3 + \ldots$$

where $\psi_1, \psi_2, \ldots \psi_n$ have the properties :—

(1) $\psi_n = 0$ when $\beta = 0$, over the rest of the plane $z = 0$,

(2) $\partial \psi_n / \partial \alpha = 0$ when $\alpha = 0$, over the annulus,

and all the conditions of our problem will be satisfied.

We find

$$\frac{\partial^2 \psi_{n+1}}{\partial \alpha^2} + \frac{\partial^2 \psi_{n+1}}{\partial \beta^2} = - \left\{ \cos \beta \frac{\partial}{\partial \alpha} \cosh \alpha \frac{\partial}{\partial \alpha} + \cosh \alpha \frac{\partial}{\partial \beta} \cos \beta \frac{\partial}{\partial \beta} \right\} \psi_n,$$

where no complementary function satisfying $\dfrac{\partial^2 \psi_{n+1}}{\partial \alpha^2} + \dfrac{\partial^2 \psi_{n+1}}{\partial \beta^2} = 0$ must be

added at any stage. It is understood that this development of the solution is only valid near the annular surface.

Proceeding to the successive approximations,

$$\frac{\partial^2 \psi_1}{\partial \alpha^2} + \frac{\partial^2 \psi_1}{\partial \beta^2} = -\left\{ \cos \beta \frac{\partial}{\partial \alpha} \cosh \alpha \frac{\partial}{\partial \alpha} + \cosh \alpha \frac{\partial}{\partial \beta} \cos \beta \frac{\partial}{\partial \beta} \right\} e^{-\alpha} \sin \beta$$

$$= \tfrac{1}{4} \sin 2\beta,$$

whence $\psi_1 = -\tfrac{1}{8} \sin 2\beta$, and the second approximation to ϕ is

$$\phi = e^{-\alpha} \sin \beta - \frac{a}{8c} \sin 2\beta.$$

Again,

$$\frac{\partial^2 \psi_2}{\partial \alpha^2} + \frac{\partial^2 \psi_2}{\partial \beta^2} = + \tfrac{1}{8} \left\{ \cos \beta \frac{\partial}{\partial \alpha} \cosh \alpha \frac{\partial}{\partial \alpha} + \cosh \alpha \frac{\partial}{\partial \beta} \cos \beta \frac{\partial}{\partial \beta} \right\} \sin 2\beta$$

$$= -\tfrac{1}{8} \cosh \alpha \, (\sin \beta + 3 \sin 3\beta),$$

whence $\qquad \psi_2 = \tfrac{1}{64} \cosh \alpha \, (3 \sin 3\beta + 4\beta \cos \beta),$

and the third approximation is

$$\phi = e^{-\alpha} \sin \beta - \frac{a}{8c} \sin 2\beta + \frac{a^2}{64c^2} \cosh \alpha \, (3 \sin 3\beta + 4\beta \cos \beta).$$

We do not proceed further, as the general term cannot be recognised. On the surface $\alpha = 0$,

$$\phi = \phi_0 = \sin \beta - \frac{a}{8c} \sin 2\beta + \frac{a^2}{64c^2} \, (3 \sin 3\beta + 4\beta \cos \beta)$$

$$-\left(\frac{\partial \phi}{\partial n}\right)_0 = \frac{1}{a}$$

from which the kinetic energy can be found. If σ is the density of the liquid, the whole kinetic energy of the liquid is T, where

$$2T = -2\sigma \iint \phi_0 \left(\frac{\partial \phi}{\partial n}\right)_0 dS$$

taken over one side of the annulus. Thus if ϕ, $\partial\phi/\partial n$ are multiplied by aU, where U is the velocity of the annulus,

$$T = 2\pi\sigma aU^2 \int_{c-a}^{c+a} \rho \, d\rho \, \phi_0.$$

But on the surface,

$$\rho = c + a \sqrt{(1-\mu^2)} = c + a \cos \beta, \qquad d\rho = -a \sin \beta \, d\beta,$$

and $\qquad T = 2\pi\sigma a^2 U^2 \int_0^\pi \sin \beta \, (c + a \cos \beta) \, \phi_0 \, d\beta,$

or $\qquad T = 2\pi\sigma a^2 U^2 \, (T_1 + T_2 + T_3 + T_4)$

where

$$T_1 = \int_0^\pi \sin^2 \beta \, (c + a \cos \beta) \, d\beta = \tfrac{1}{2} \pi c,$$

$$T_2 = -\frac{a}{4c} \int_0^\pi \sin^2 \beta \cos \beta \, (c + a \cos \beta) \, d\beta = -\frac{\pi a^2}{32c},$$

$$T_3 = \frac{3a^2}{64c^2} \int_0^\pi (3 \sin^2 \beta - 4 \sin^4 \beta)(c + a \cos \beta) \, d\beta = 0,$$

$$T_4 = \frac{a^2}{16c^2} \int_0^\pi \beta \sin \beta \cos \beta \, (c + a \cos \beta) \, d\beta$$

$$= \frac{a^2}{64c^2} \int_0^\pi \beta \, (2c \sin 2\beta + a \sin 3\beta + a \sin \beta)$$

$$= \frac{a^2}{64c^2} \left[\beta \left(-c \cos 2\beta - \frac{a}{3} \cos 3\beta - a \cos \beta \right) \right]_0^\pi$$

$$+ \frac{a^2}{64c^2} \int_0^\pi d\beta \left(c \cos 2\beta + \frac{a}{3} \cos 3\beta + a \cos \beta \right)$$

$$= -\frac{\pi a^2}{64c^2} \left(c - \frac{4a}{3} \right),$$

or to relative order a^2/c^2,

$$T = \pi^3 \sigma a^2 c U^2 \left(1 - \frac{3}{32} \frac{a^2}{c^2} \right).$$

Series of zonal harmonics for the value of ϕ at any point can easily be obtained by the reader, making use of the method already adopted.

It is evident that the corresponding electrical problem, for which this value of ϕ holds, is that of an annular opening in an infinite plane conductor. The surface densities σ of the free distribution on the two portions of the conductor, when at the same potential, are given by $(ac)^{-1}(\partial \phi / \partial \beta)_{\beta=0}$, being infinite at each edge, or

$$a \zeta \sigma = \cosh \alpha - \sinh \alpha - \frac{a}{4c} + \frac{13}{64} \frac{a^2}{c^2} \cosh \alpha.$$

On the inner surface,

$$\cosh \alpha = \sqrt{(1 + \zeta^2)} = \frac{c - \rho}{a},$$

$$\sinh \alpha = \zeta = \frac{1}{a} \sqrt{(c - a - \rho)(c - a + \rho)},$$

and on the outer,

$$\cosh \alpha = \sqrt{(1 + \zeta^2)} = \frac{\rho - c}{a}, \quad \sinh \alpha = \zeta = \frac{1}{a} \sqrt{\{(\rho - c - a)(\rho - c + a)\}}$$

and the surface densities can be written down. It is an interesting, though obvious, matter to work out the capacity of such an arrangement, by the method previously adopted for the capacity of an annulus.

A Study of the Balance.

By A. E. Conrady, Professor of Optical Design at the Imperial College.

This research was not undertaken with the deliberate aim of exceeding the precision of mass-determinations as carried out in the great institutions specially devoted to this subject. I should have considered it both presumptuous and hopeless to attempt such a feat, and should probably have abandoned my studies at an early stage if it had not fortunately happened that the decisive part of my work had been completed before I came across comparable results obtained elsewhere. It was only then that I realised that the methods evolved had led to a very considerable diminution of the residual errors of weighings, in spite of the inexpensive instrument employed and of the primitive conditions under which the observations were made.

A projected series of experiments called for weighings of small masses, up to perhaps 50 grm., within 0·1 mgrm. As I did not possess a balance, I bought the least expensive type of analytical balance, one by Sartorius, to carry 200 grammes in each pan, with a triangular phosphor-bronze beam, 14 cm. long, with agate knife-edges and plane bearings, with a complete arrestment for beam, suspensions, and pans, and with a rider-scale divided to read directly to 0·2 mgrm. by the usual centigramme-rider. The cost at the time (1905) was £6. The balance was described in the catalogue as "sensitive to 0·2 mgrm.," but I trusted that the required accuracy within 0·1 mgrm. would be obtainable by using the more refined weighing methods of the physical laboratory.

Naturally, the first work undertaken consisted in determining the errors of the set of analytical weights to be used with the balance. The plan described in Kohlrausch's 'Practical Physics' was adopted, and the simple Gaussian method of exchange was used so as to eliminate the index error and the inequality of the arms of the balance. The observations were reduced within 0·01 mgrm. with occasional retention of 0·005 mgrm. This first calibration had been begun within one hour of the time when the balance had been taken to pieces in the room in which it was stored and re-erected in another room. On consideration of the fundamental nature of the work, this procedure appeared to cast grave doubts upon the reliability of the results. The eight comparisons of the brass weights were therefore repeated a week later, the balance and weights having been given three hours to settle down to the temperature of the surroundings before observations were commenced. The

method of double exchange was used (first, A in left pan ; second, B in left pan ; third, A again in left pan), in order to eliminate also changes of the zero-point so far as they are proportional to elapsed time. When these observations were reduced the surprising and entirely unexpected result emerged that the greatest disagreement with those of the previous calibration was only 0·01 mgrm. (on the actual weighings, not on the deduced errors of individual pieces), and that the probable error of one weighing—all treated as of equal reliability—was of the order of 0·004 mgrm., or one-fiftieth of the possible discrepancy suggested by the makers of the balance.

It was this high precision of the first results obtained from the balance which caused me to postpone the projected experiments, and to make the balance itself the subject of further study. It appeared probable that still better results might be obtained by improvements in the adjustments and by more care in the actual observations. A long series of experimental weighings was thus begun, but for 1½ years no progress whatever was made in the accuracy of the results. The probable error derived from any reasonably extensive series of weighings remained with singular obstinacy in the neighbourhood of the value 0·004 mgrm. originally found, in spite of the fact that a succession of refinements applied to the instrument and to the methods of observation and reduction were without exception of a kind which must greatly diminish the effects of the sources of error at which they were aimed. This led to a growing conviction that there must be present some source of error of greatly preponderating magnitude which had escaped detection. This conviction was strengthened by the fact that occasionally the results of a series of weighings were decidedly worse than usual, and led to a note in the journal: "Balance evidently in bad condition," the observer being included in the indictment in one or two instances.

Eventually a bad case of this kind led to the discovery of the elusive preponderating source of error. The knife-edges, being made of material of limited strength and rigidity, necessarily do not terminate in an absolutely sharp edge, but have a finite radius of curvature of the order of 0·01 mm. As a consequence, the effective length of the lever-arm at which the load is applied would change if the plane resting on a terminal knife-edge were rigidly attached to the pan, and if the weight in the latter were put into varying positions in successive exchanges, for the planes would then become tilted, and the contact line would shift (fig. 1). To avoid this well-known source of error all balances have an "intermediate joint" between the suspension and the pan, so that the latter can swing independently of the former. In the Sartorius balances the joint primarily relied upon for this purpose takes the form of two round pins at the upper end of the stirrup

from which the pan is suspended, these pins resting in larger holes in the lower ends of the fitting attached to the agate plane. If the fulcrum thus
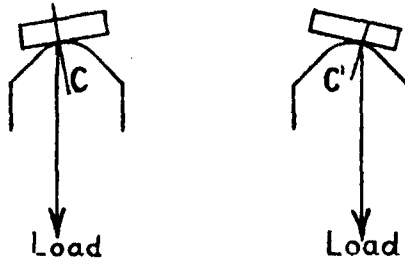

Fig. 1.—Tilted end-planes cause change of lever arms.

provided were a definite and frictionless one it would ensure that the load itself would force the agate plane always into the same orientation with reference to the horizon. But as the pins are over 1 mm. in diameter and rest in holes of about 2 mm. diameter, they may take any position within the sliding angle of friction of 5°, or more, from the really lowest point of the
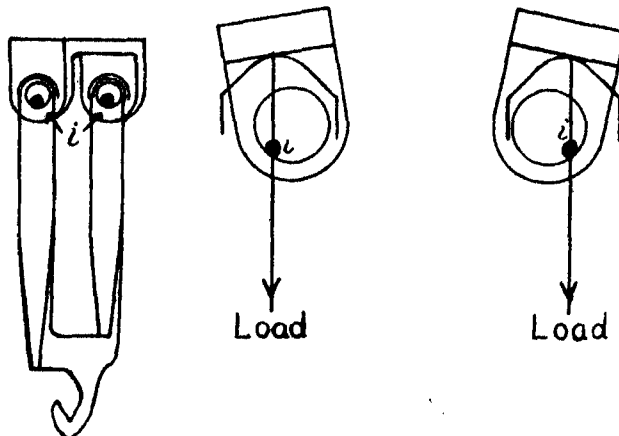

Fig. 2.—Sartorius intermediate joint allowing end-planes to tilt.

hole, and so become themselves a cause of tilted end-planes instead of preventing such tiltings.

This defective intermediate joint was definitely identified as the source of the large errors, the aggravation occurring when the stirrup happened to rest with friction against one of the cheeks of the upper fitting. The cure applied consisted in rendering the original intermediate joint immovable by tightly screwing its two parts together, and in relying on the hook at the lower end of the stirrup as a more definite and efficient intermediate joint.

As soon as this change had been made, the probable error of the observa-

tions for a calibration of a set of decigramme weights went down to 0·0013 mgrm., or to one-third of the previous value. Each complete weighing in this set consisted of four partial weighings—

(1) A in left pan,
(2) B in left pan,
(3) B again in left pan,
(4) A in left pan,

and the sensitivity was determined at frequent intervals by a fifth observation with a suitable added load produced by a shift of the rider. The latter weighed 1 mgrm., and was not shifted during the four partial weighings.

The discussion of the residuals of this series immediately revealed another but much smaller systematic error. It was found that the sign of the residual error of any one complete observation depended very decidedly on the sequence of the deflections of the pointer in the partial weighings. If at the first partial weighing the deflection was larger than at the second, the difference A–B tended to be found too small, and conversely in the reverse case. This was tentatively attributed to the imperfect elasticity of the knife-edges and of their bearings. These must be—on account of the extremely short radius of curvature—loaded almost to the limit of elasticity. Hence the deformation (" flattening ") of the edge produced by the load in any one observation would disappear only partially on arrestment, the residue of deformation remaining for a considerable period. The consequence must be that the balance retains during that period a bias in favour of the previous position of rest and gives a false reading at the succeeding observation. This led to an effort to devise a sequence of partial observations which would defeat this bias of the balance. An obvious method would be to take advantage of the light rider and its finely divided scale, and to find by a series of approximations such an addition by ridershift to the lighter mass that eventually the deflections in successive exchanges would be practically identical. That method, however, would call for several wasted observations. The method really adopted, and adhered to ever since, was a simple modification of the well-known series of four partial weighings already referred to, the object being to attach the " bias " twice in one sense and twice in the opposite sense to the partial results, and so to cause its complete cancellation in the mean of all four.

Assuming that the residual difference of the two masses A and B is so small (or has been so adjusted) as to keep the variation of deflection on exchange within practicable limits, a wasted observation—not recorded— is first made with B in the left pan to adapt the knife-edges to the

load and to establish the corresponding bias. Then follow the four real observations :—

(1) A in left pan, deflection D_1, which is at once determined from the pointer readings.

(2) B in left·pan, deflection D_2, also determined immediately after the readings of the pointer. D_2 will of course closely correspond to the deflection in the preliminary observation.

(3) B still in left pan, but with such an addition by ridershift, easily calculated from the known sensitivity, as will cause the deflection to become as nearly as possible equal to D_1.

(4) A in left pan, but with such a ridershift as will cause the nearest possible approach to deflection D_2.

By observation (1) A–B is obtained, afflicted with the bias produced by a change from previous deflection D_2 to new deflection D_1. By observation (3) B–A is obtained, afflicted by the same bias as observation (1), but attached to the reversed position of the two masses. Hence the difference (1)—(3) will give 2 (A–B), but the bias cancels out. The same argument applies to the combination of observations (2) and (4). The set of four observations simultaneously cancels any progressive change in the balance during the time required for the complete set, which in my case was about 12 minutes.

The preliminary wasted observation was usually omitted, as it was found that the small systematic error (less than 0·001 mgrm.) aimed at was sufficiently removed by making only the four actually used partial weighings.

The first trial of this method on the same set of decigramme-weights gave a probable error of one complete weighing of 0·0008 mgrm., or only one-fifth of the original error and less than two-thirds of the one obtained without the refinement of the "alternating position of rest."

Up to this stage of the experiments the balance had been used in the usual laboratory way, the pointer being read with the aid of a fixed lens of 5 inches focal length, and the sliding door of the balance being sufficiently opened during the exchanges to allow of the use of a long forceps. The latter, however, was of such length that the warm hand remained entirely outside the balance case. In spite of this precaution air-currents induced by the use of the sliding door appeared to be largely responsible for the residual errors. Decidedly crude arrangements were therefore made, which allowed the balance case to remain closed all the time, the loads being handled by the original long forceps attached to the case by a washleather conical tube. A considerable number of calibrations of sets of weights was

then carried out, and gave probable errors of one complete weighing ranging from 0·0005 down to 0·0003 mgrm.

It may be briefly stated that practically all the experiments were carried out on sets of weights, mostly fractions of a gramme, of the pieces 1, 2, 3, 4 and 5. Comparison of these among themselves and with 10, the unit of the next decade, gives twelve different combinations: $1 + 2 = 3$, $1 + 3 = 4$, $1 + 4 = 5$, $2 + 3 = 5$, $2 + 3 = 1 + 4$, $2 + 4 = 1 + 5$, $3 + 4 = 2 + 5$, $1 + 2 + 3 + 4 = 10$, $1 + 4 + 5 = 10$, $2 + 3 + 5 = 10$, $2 + 4 + 5 = 10 + 1$, $3 + 4 + 5 = 10 + 2$. If the first two comparisons are repeated a second time, fourteen observations result, the normal equations of which are direct solutions for the five corrections as the mean of ten observations in the case of the pieces 1, 2, 3 and 4, and as the mean of eight observations in the case of 5. Owing to the large number of observations a good determination of the probable error is secured; the great variety of combinations moreover renders it unlikely that any systematic error should remain undetected. Mere repetitions of the same comparison, done always in the same way, are apt to give quite fallacious ideas as to the accuracy attained.

About the time when my work had reached the stage described, a volume of "Travaux et Mémoires" of the International Bureau at Breteuil appeared, in which results of comparable calibrations of weights are given. The probable error for small weights up to 1 grm. ranges from about 0·0015 to 0·003 mgrm. for one complete weighing; it is, therefore, on an average, five times as large as the one I reached with my comparatively heavy balance. The load on the central knife-edge of my balance was about 110 grm. when very light aluminium pans were employed for comparisons of small weights. The Breteuil weighings were made on a balance specially constructed for loads not exceeding 1 grm., and the whole of the moving parts probably weighed less then 10 grm. I have only come across one authenticated set of weighings, also for fractions of a gramme, which gives a much lower probable error than that secured at Breteuil. This set is mentioned in a note in "Zeitschrift für Instrumentenkunde," from the Berlin Institute of Weights and Measures, and leads to a probable error of 0·0008 mgrm., or twice that in my final observations. The balance used was of the same type as that employed at Breteuil. · Both the Breteuil and the Berlin observations were made telescopically from a considerable distance.

As it seemed desirable to confirm the conclusions at which I had arrived, I bought another very small Sartorius balance with a beam only 8 cm. long, " to carry 10 grm. in each pan, and sensitive to 0·1 mgrm." This showed the same inconstancy as the 200 grm. balance until the intermediate joint of the suspensions was rendered immovable. It then yielded results by the

method of alternating deflections of even higher precisions than the heavier balance, probable errors down to a little over 0·0001 mgrm. being repeatedly recorded. An even more satisfactory confirmation of my· conclusions was obtained from a rough "bullion-balance" for loads up to 1 kilo. This was fitted with plane bearings (the original ones were roof-shaped), and with suspensions designed to minimise the effects of the finite radius of the terminal knife-edges,. also with a crude but reasonably draughtproof case. It thus became an extremely satisfactory precision balance on which heavy weights can be compared well within 0·01 mgrm.

Shortly before the outbreak of the Great War, Sir Richard Glazebrook kindly consented to have some experiments made with my original balance in the constant-temperature rooms at the N.P.L., the balance having in the meantime been fitted with mirror and telescope, so as to allow of its use on a distant scale with a greatly increased deviation per milligramme. The suspensions had also been further modified. It was found that masses up to 100 grm. could be compared within about 0·001 mgrm. ; I had never succeeded in doing this at my house, on account of rapid changes of temperature, vibration from traffic, and residual defects in the original suspensions. These experiments at Teddington were interrupted by the War and have not been resumed ; but I understand that my balance is largely used for weighings of great accuracy.

A number of refinements in both the balance and in the method of observation have not been mentioned in the foregoing account of my experiments ; these additional desiderata are included in the following concise account of the essential features of a balance of highest precision and of the proper method of using it. A reliable judgment in these respects can only be based upon careful *quantitative* estimates of the known sources of error. The accuracy reached and occasionally exceeded in my experiments, amounted to 7×10^{-9} of the load on the terminal knife-edges (*i.e.*, 0·001 mgrm. in 140 grm.), and to $2·5 \times 10^{-9}$ (0·001 mgrm. in 400 grm.) of the load on the central knife-edge. To render possible this degree of precision, the length of the lever-arm (70 mm. in my case) must have been "definite" within the same minute fraction ; but it might, and undoubtedly did, change proportionately to time by a large multiple of that fraction even in the 12 minutes required for one complete weighing. The important point to be noted is, however, that the supporting line of the central knife-edge must, at any given moment, be definite within $70 \times 2·5 \times 10^{-9}$, or $1·8 \times 10^{-7}$ mm. (1·8 Ångström units !), and the contact-line of the terminal knife-edges must be definite within 5×10^{-7} mm. These are the quantities on which reliable estimates may be based. Their

minuteness renders plane bearings absolutely indispensable, for, with cylindrically curved or roof-shaped bearings, a very slight lateral shift would change the contact-line by many times the permissible variation in length of arms.

The Beam.

Many elaborations found in the design of the beam are of little if any value. There should be as few joints and screws as possible, for every one of these may under changing temperature become a source of sudden minute shifts of the centre of gravity. By far the most important point is the fixing of the knife-edges. These are usually simply driven into prepared seatings In the Sartorius balances they are neatly fitted in this way, but, in addition, a cement (apparently shellac) is used to fill the interstices. My kilogramme balance originally had the steel knife-edges merely tightly driven into the aluminium beam. Repeatedly there were sudden shifts of the zero point. These were tentatively attributed to the release of strains between the knife-edges and their seatings, caused by the difference of thermal expansion. This assumption appeared to be correct, for, on a careful and sustained treatment with shellac-cement, this trouble vanished, never to return. Similar disturbances may be traced to a slightly loose or badly fitted screw taking a new position with a change of temperature. The short beam, first introduced by Bunge, has a great advantage over the formerly preferred long beam, because it is more rigid, gives a higher sensitivity at any given time of vibration, and is also less affected by inequalities of temperature.

The Knife-edges and their Bearings.

The terminal knife-edges require means for the well-known adjustments to establish parallelism with the central knife-edges, equality of the lever-arms and unchanging sensitivity with varying loads. The Sartorius arrangements for this purpose are both convenient and reliable. By far the most important one of these adjustments is that for parallelism of the projections of the three knife-edges upon a horizontal plane, for any departure from this parallelism means that the lever-arm changes according to the point of the terminal knife-edge below which the centre of gravity of the load is situated. It is difficult, if not impossible, to secure this parallelism for any length of time or for varying loads within less than 20 seconds of arc or 0.0001 radian. As the lever-arm must be definite within 5×10^{-7} mm., this defect in parallelism makes it necessary that the load shall always be applied within 0.005 mm. of a fixed point in each terminal knife-edge. Balances therefore always have in

their suspensions some kind of "cross-joint" or fulcrum with an axis at right angles to the knife-edge which is supposed to assure this adjustment of the centre of gravity of the load automatically, but rarely does so with sufficient precision. The second source of error at the terminal knife-edges arises from their finite radius of curvature of about 0·01 mm. which causes a change in the length of the lever-arms if the planes bearing on the knife-edges are tilted. The permissible tilt is found by dividing the allowable variation of the lever-arm of 5×10^{-7} mm. by the estimated radius of curvature of 0·01 mm. and is therefore 0·00005 radian or only 10 seconds of arc. None of the usual "intermediate joints" come anywhere near this degree of precision, and the jointing of the suspensions is thus recognised as the chief mechanical defect in existing balances.

My 200-grm. balance was greatly improved and yet simplified by combining the "cross joint" and the "intermediate joint" into one. A rigid stirrup was attached to the original holder of the agate plane and fitted with a conical and glass-hard steelpoint on the horizontal part from which the pan was suspended by a polished concave steel cup. The radius of curvature of a hard steelpoint capable of carrying more than 100 grm. is, however, at least 0·1 mm., and assuming a sliding angle of friction of about 6°, the exact point of application of the load remains in doubt to the extent of about 0·01 mm. in any azimuth, which is twice the calculated tolerance in the direction of the knife-edge, and corresponds, with the steelpoint at about 40 mm. below the knife-edge, to a possible tilt of the plane by 0·01/40 = 0·00025 radian, or five times the calculated limit of 0·00005. Nevertheless these modified suspensions proved vastly superior to the far more complicated original

Fig. 3.—Single point intermediate joint.

ones and rendered possible the excellent results with heavy loads secured at the N.P.L. A few discordant results were, however, almost certainly due to a specially eccentric position of the steel cups causing the maximum dislocation of the point of application of the load and so greatly exceeding the permissible amount.

A further refinement of the same idea was applied to the kilogramme balance by using a steel point of the same type on the stirrup, but providing a separate arrestment, which lifts the steel bearing from which the pan is suspended, and so allows of making this bearing practically plane without risk of accidental derangement. This appears to be the best and most complete solution of the suspension problem.
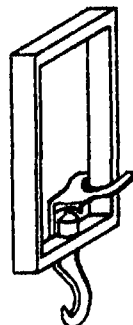
The Arrestment.

The essential features of the arrestment are that the suspensions and the beam should be gently and steadily lifted off the terminal knife-edges and the central bearing respectively, and that they should be replaced in exactly the same relative positions as before when the arrestment is again released. Freedom of the arresting bar to make slight movements in the horizontal plane is particularly objectionable, because the suspensions will then be placed upon the knife-edges in various positions in different partial weighings, and the point of application of the terminal loads will shift accordingly and cause a change of length of the lever-arm. The Mendeléeff type of arrestment, with arms swinging round an axis in line with the central knife-edge, appears to be the best, and the form given to it by Sartorius gives very satisfactory results, which, however, would be rendered still more definite if the compass joint at the centre were replaced by a strictly geometrical bearing such as is used by Sartorius at the supporting points of beam and suspensions.

An extremely trying defect of all arrestments is the adhesion of one or other of the supporting points to its counterpart, which causes one end of the beam to be pulled down a certain distance and then released with a jerk. Good results cannot be obt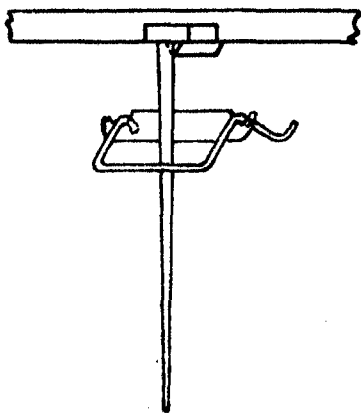ained when the arrestment develops this defect, and the balance must be taken to pieces and all the contact points cleaned (suitably shaped sticks of dry elder pith are best for the purpose) before proceeding. This had to be done quite frequently in the course of my experiments, but towards their end I devised a simple addition to the arrestment which is an absolute preventive of this trouble, namely, a very gentle "brake" applied to the pointer which is only lifted off at the end of the releasing movement of the arrestment. The "brake" consists of a light bent wire hanging from a supporting edge attached to the pillar, one end of the wire having a projecting end which is depressed by the arrestment when in its lowest position.

FIG. 4.—"Brake." A bent wire resting on the pointer keeps the balance steady until arrestment is completely released.

The horizontal part of this wire bears with a force of about a centigramme on the pointer and keeps the balance steady until the beam and suspensions are quite out of contact with the supporting points. The result is that, even when the latter are slightly adhesive, the balance starts its

oscillations from its actual position of rest, and that a perfectly definite arc of vibration becomes associated with any given difference of the two loads. This is essential for the complete elimination of errors arising from the irregular curvature and imperfect elasticity of the knife-edges.

An extremely serious result of the action of the arrestment is that the knife-edges and their bearings come together, always in precisely the same relative position, with a finite velocity and, therefore, with a certain sudden, though minute, impact. The consequence is that the knife-edges gradually develop a distinct flat facet at the corresponding contact lines—utterly invisible, even under the highest powers of the microscope, but easily demonstrated by observation of the balance near the critical central part of its scale. When carefully adjusted and gently released, a balance will remain still in the position in which the arrestment leaves it, and will refuse to leave that position with an overweight in one pan which, in much-used analytical balances, may reach and even exceed a whole milligramme. In my small Sartorius balance, which had had very little and decidedly careful use, the necessary overweight was recently found to amount to 0·02 mgrm., which at any other part of the scale would cause a change of pointer reading by about a whole scale division. The corresponding width of the flat facet of the central knife-edge (which is the chief offender) comes out at about 1/60,000th of a millimetre, and is therefore far beyond the limit of microscopical resolving power.

Although the existence and magnitude of this grave source of error were only discovered after the completion of my experimental weighings, I fortunately escaped its effects because I reached the empirical conclusion in the earliest stages that good results were only obtainable if the time-honoured method of letting the balance swing to both sides of the central position in any one observation were abandoned, and if, instead, an ample overweight on one side or the other were permanently applied, so as to secure elongations entirely to either the right or the left side of the centre of the scale. Owing to the very pronounced damping effect resulting from the high sensitivity employed, coupled with the careful avoidance of any initial impulse, all my observations were thus made on those parts of the knife-edges which lie outside the flat facet and which consequently have a reasonably uniform curvature. It seems advisable to fit the finest balances with an auxiliary device, on similar principles to that of my " brake," which, before the lifting of the brake, would push the beam into a position slightly tilted towards the side of the scale on which the readings are to be taken, thus making absolutely sure of the avoidance of this source of error.

The Rider and its Scale.

The method of the alternating position of rest which, according to my experiments, must be employed to secure the highest possible precision in mass determinations, requires very close adjustment of the equilibrium. This is only attainable by a light rider upon a finely subdivided scale. It is a remarkable fact that it has for some considerable time been accepted as an axiom by the great Continental metrological institutions that riders are inadmissible for their balances. As an inevitable consequence, the latter do not admit of eliminating the errors due to irregular curvature and imperfect elasticity of the knife-edges, and therefore cannot reach the highest precision. The objection to the rider is that its weight-value is not nearly so definite as that of a weight in one of the pans. But I found by direct experiment with heavy riders that my 200-grm. balance had a probable error of the rider position of only 0·0001 of the rider-weight; therefore, with the really used rider weighing 1 mgrm., the probable error from this source was only 0·0001 mgrm. for one partial weighing, and quite unimportant when compared with the probable error of one complete weighing of not less than 0·0003 mgrm. It is, however, necessary to state that accuracy to 0·0001 of the rider-weight will only be obtained if the rider is placed squarely upon a scale divided by sharp and clean lines, so that the rider actually rests in the V-shaped notches of the scale-divisions. A lens magnifying three or four times should be attached to the rider-shifter, so that the exact position of the rider can be sharply observed.

General Requirements.

The case in which the balance is enclosed should, of course, be draught-proof and would probably be greatly improved if it consisted almost entirely— including the foundation-plate—of thick and well-polished aluminium, so as to equalise the internal temperature. A separate inner case surrounding the beam is highly desirable. To avoid errors from radiation pressure, the illumination should be as restricted and as symmetrical as possible. The deflections are undoubtedly best determined by the reflecting method. All my principal experiments were made by direct pointer readings, the sensitivity being 12·5 divisions of approximately 1 mm. to a milligramme. One-fiftieth of a division was estimated and the good results obtained were due to my possessing the knack of mentally subdividing a scale to perhaps an unusual degree, my probable accidental error being decidedly less than 0·01 of a division. I was also assisted by the fact that the method of alternating deflection very largely eliminates the well-known systematic error of " personal scale," for example, the habit of always reading 0·56 when a micrometer microscope would give 0·54.

The Autostatic State of a Balance.

When I first realised that I had reached an apparently unprecedented degree of precision in weighings, I felt compelled to examine minutely the whole method of observation and reduction employed, because I was myself highly sceptical as to the reality of the advance. Every detail bore the tests which I applied, with the exception of one which perturbed me for a long time : It was easily concluded, on the ordinary principles of statics, that if the level of the balance-case were to vary in the course of a set of partial weighings by only a few seconds of arc, this tilt alone would produce the whole of the probable error actually arrived at as including *all* sources of error. The balance was supported on the strongest side of the outer packing case in which it had originally arrived, the case being firmly screwed to a wall of the observing room. It seemed quite unthinkable that the table so formed should be firm within the minute limit called for. Eventually the solution of this mystery was found, and was subsequently deliberately applied, in order to secure extremely high accuracy with the 10-grm. balance when used on an ordinary dining table :—

In a sensitive short-beam balance, the centre of gravity of the moving parts lies only a very small fraction of a millimetre below the axis around which the balance oscillates. If the central knife-edge were absolutely sharp, the beam would, nevertheless, take a definite orientation with reference to the true horizon, no matter how the balance case were tilted, and the pointer would therefore correctly indicate this tilt, and the weighings would be correspondingly falsified. The central knife-edge, however, is really a cylinder of about $0{\cdot}01$ mm. radius, and the beam swings round the axis, C (fig. 5), of this cylinder. The balance will be in stable equilibrium if the centre of gravity, G, of the moving parts is below the axis, C, of rotation, and there are three classes of cases. If G is also below the supporting plane (fig. 5*a*), then a tilt of the whole balance, say
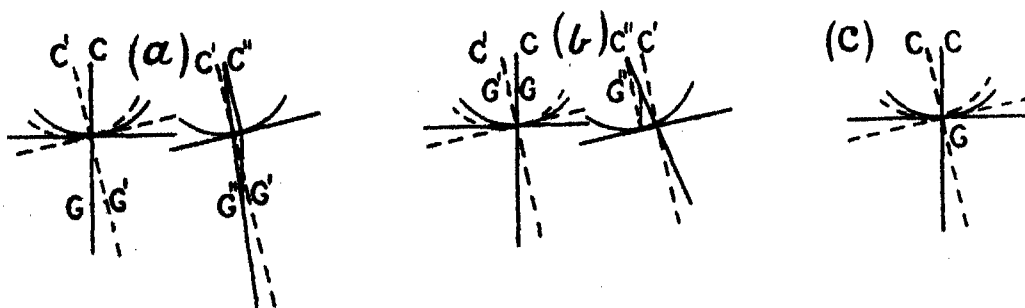

Fig. 5.—Effects of tilting the balance case.

towards the left, will shift the centre of gravity to a point to the right of a vertical plane, passing through the contact-line, and the balance will swing towards its previous orientation with reference to the horizon, but will not reach it, because the rolling of the edge on the supporting plane will bring the contact-line vertically over G before that orientation is reached. The balance, therefore, is less sensitive to tiltings of its case than one playing on an absolutely sharp knife-edge. If G is above the supporting plane, then a tilt of the case towards the left will also carry G to the left of the vertical plane of the contact-line, and the beam will swing in the direction of the tilt—exactly contrary to what one would expect—fig. 5*b*. Finally, if G lies in the contact-line, then tiltings of the case will not affect the pointer-readings at all, because the movable mass remains concentrated on the contact-line, and produces no turning moment. I propose to call this remarkable special case of balance-adjustment the "autostatic state," for a balance so adjusted gives pointer-readings which are unchanged by tiltings of the case, and are therefore independent of the *direction* of the force of gravity.

The explanation of the high accuracy obtained on the infirm support of my balance was found to be that the autostatic state was very nearly realised at the sensitivity employed in the experiments. This was not purely luck, for the sensitivity had been fixed at the selected value because it gave the most consistent results, but without any knowledge of the reason why it should do this.

As the distance CG can be easily calculated from the mass of the moving parts and the sensitivity, the experimental production of the autostatic state is the easiest method of determining the radius of curvature of the central knife-edge. The experiment consists simply in taking the position of rest, then tilting the case by shortening say, the left, and lengthening the right footscrew, and noting whether the pointer moves in the direction which simple statics would lead one to expect, or in the opposite direction. In the first case the sensitivity must be increased by the gravity-bob, in the second diminished. The autostatic adjustment is thus quickly found. For balances on any but the firmest foundation, the autostatic adjustment is a highly desirable safeguard. It is applicable to balances read by microscopes or by reflection, provided that both scale and reading device are attached to the balance case. Balances with separately mounted scales and reading telescopes or lightspots are always placed on such firm foundations that the autostatic adjustment would not lead to any sensible gain in precision.

Monoclinic Double Selenates of the Manganese Group.

By A. E. H. Tutton, D.Sc., M.A., F.R.S.

Only three salts are included in this group of the series $R_2M(SeO_4)_2 . 6H_2O$ in which M is manganese, namely, those in which R is rubidium, cæsium, and ammonium, the potassium salt having resisted all attempts at preparation. It will be remembered that the corresponding hexahydrated potassium manganese sulphate has also never been obtained, and appears to be incapable of existence, for even at $0°$ C. the tetrahydrated salt forms instead. Hence, it is still more improbable that the hexahydrated potassium manganous selenate can exist. In all the author's attempts to prepare it, crystals resembling a dihydrated double selenate of potassium and manganese described by Topsøe were obtained instead.

The rubidium and cæsium salts of the group are now described for the first time. Crystals of the ammonium salt were obtained by von Hauer and measured by Topsøe,[*] who also determined their density. But no optical investigation of ammonium manganous selenate has hitherto been undertaken, this salt not being included by Topsøe and Christiansen in their well-known research.

The solution of manganous selenate used in preparing the double salts was obtained by digesting for several days, at the ordinary temperature in a covered vessel, excess of specially pure manganous carbonate with a measured quantity of the pure selenic acid prepared for this research by Messrs. Hopkin and Williams. The emulsion was finally filtered and the clear filtrate, consisting of a solution of manganous selenate, was divided into three portions, and each mixed with a solution of the calculated equi-molecular quantity of the alkali selenate, in one case rubidium selenate, in another case cæsium selenate, and in the third case ammonium selenate. These three latter alkali selenates were prepared as described in previous communications.

Excellent crystals, clear and transparent with a faint pink colour, were obtained by slow spontaneous evaporation at ordinary temperature and pressure, and numerous crops were obtained on successive days, from which the most perfect individual crystals were selected for the purpose of this research.

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[*] Haldor Topsøe, ' Krystallogr.-kem. Unders. o. de Selensure Salte,' Copenhagen, 1870.

Rubidium Manganese Selenate, $Rb_2Mn(SeO_4)_2 . 6H_2O$.

Crystal System.—Monoclinic. Class No. 5, holohedral-prismatic.

Axial Angle.—$\beta = 105°\ 9'$.

Ratio of Axes.—$a : b : c = 0.7422 : 1 : 0.5008$.

Forms observed.—$a\{100\}$, $b\{010\}$, $c\{001\}$, $p\{110\}$, $p'\{120\}$, $p''\{210\}$, $p'''\{130\}$, $q\{011\}$, $r'\{\bar{2}01\}$, $o'\{\bar{1}11\}$.

Habit.—Typically that of a rubidium salt of the series, characterised by moderate and often nearly equal-sized faces of $q\{011\}$ with respect to those of $c\{001\}$. Two typical crystals are shown in figs. 1 and 2. The crystals of most of the crops were more or less tabular parallel to $c\{001\}$, as shown in fig. 2, but a few crops showed a more nearly prismatic habit, as indicated in the simple crystal represented in fig. 1.
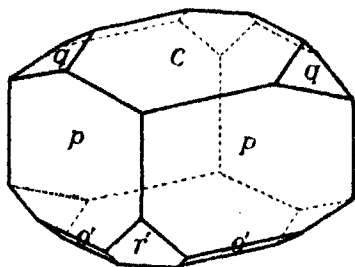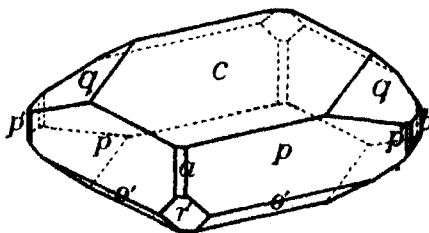

Fig. 1.　　　　　Fig. 2.

Typical crystals of rubidium manganese selenate.

The faces of $c\{001\}$, $q\{011\}$, and $p\{110\}$ were usually the only ones well developed. Occasionally those of $r'\{\bar{2}01\}$ were fairly prominent, and those of $o'\{\bar{1}11\}$ clearly visible, as in fig. 1. But the faces of $a\{100\}$, $b\{010\}$, $p'\{120\}$, $p'''\{130\}$, and $p''\{210\}$ were always very narrow, usually mere lines, especially the two last mentioned forms. Fig. 2 shows a crystal exhibiting clearly all but these last two forms.

The crystals possessed a faint pink colour, and were beautifully transparent. The table of angular measurements is given on the next page.

Cleavage.—There is a good cleavage parallel to $r'\{\bar{2}01\}$.

Relative Density.—Six determinations were made by the immersion method using methylene iodide and benzene mixture.

I. Density for	16°·1/4°	......	2·7615	For 20°/4°	......	2·7604
II.	„	16°·4/4°	......	2·7618	„	......	2·7608
III.	„	16°·8/4°	......	2·7642	„	......	2·7633
IV.	„	16°·6/4°	......	2·7638	„	......	2·7629
V.	„	16°·2/4°	......	2·7659	„	......	2·7649
VI.	„	16°·3/4°	......	2·7657	„	......	2·7652

Mean ...... 2·7629

Accepted value for 20°/4°.........**2·763**.

Interfacial Angles of Rubidium Manganese Selenate.

Angle.	No. of measurements.	Limits.	Mean observed.	Calculated.	Diff.
ac = (100) : (001)......	4	74 39– 74 52	74 43	74 51	8
as = (100) : (101)......	—	—	—	45 52	
sc = (101) : (001)......	—	—	—	28 59	
cr′ = (001) : (2̄01)......	18	63 22– 63 48	63 33	63 35	2
cs′ = (001) : (1̄01)......	—	—	—	38 20	
s′r′ = (1̄01) : (2̄01)......	—	—	—	25 15	
r′a = (2̄01) : (100)......	4	41 30– 41 56	41 42	41 34	8
r′c = (2̄01) : (001̄)......	19	116 12–116 43	116 27	116 25	2
ap = (100) : (110)......	2	35 29– 35 43	35 36	35 38	2
ap″ = (100) : (210)......	—	—	—	19 43	
p″p = (210) : (110)......	1	—	15 51	15 55	4
pp′ = (110) : (120)......	2	19 27– 19 37	19 32	19 28	4
p′p‴ = (120) : (130)......	2	9 53– 10 2	9 58	9 57	1
p′b = (120) : (010)......	—	—	—	34 54	
pp‴ = (110) : (130)......	1	—	29 30	29 25	5
p‴b = (130) : (010)......	—	—	—	24 57	
pb = (110) : (010)......	2	54 24– 54 29	54 26	54 22	4
pp = (110) : (1̄10)......	23	71 4– 71 27	71 15	*	
pp = (110) : (1̄10)......	23	108 32–108 57	108 45	108 45	0
cq = (001) : (011)......	41	25 39– 25 57	25 48	*	
qb = (011) : (010)......	—	—	—	64 12	
qq = (011) : (01̄1)......	21	128 14–128 39	128 24	128 24	0
ao = (100) : (111)......	—	—	—	49 4	
oq = (111) : (011)......	—	—	—	27 19	
aq = (100) : (011)......	—	—	—	76 23	
qo′ = (011) : (1̄11)......	—	—	—	34 33	
o′a = (1̄11) : (100)......	—	—	—	69 4	
co = (001) : (111)......	—	—	—	34 35	
op = (111) : (110)......	—	—	—	43 9	
cp = (001) : (110)......	40	77 35– 77 55	77 44	*	
po′ = (110) : (1̄11)......	5	57 31– 57 47	57 40	57 44	4
o′c = (1̄11) : (001̄)......	5	44 28– 44 48	44 36	44 32	4
pc = (110) : (001̄)......	40	102 3–102 29	102 16	102 16	0
bn = (010) : (121)......	—	—	—	54 18	
no = (121) : (111)......	—	—	—	15 56	
bo = (010) : (111)......	—	—	—	70 14	
os = (111) : (101)......	—	—	—	19 46	
bo′ = (010) : (1̄11)......	—	—	—	65 17	
o′s′ = (1̄11) : (1̄01)......	—	—	—	24 43	
o′o′ = (1̄11) : (1̄1̄1)......	—	—	—	49 26	
sq = (101) : (011)......	—	—	—	38 2	
qp = (011) : (1̄10)......	40	86 14– 86 42	86 28	86 26	2
ps = (1̄10) : (1̄01)......	—	—	—	55 32	
pq = (1̄10) : (01̄1)......	40	93 21– 93 43	93 31	93 34	3
s′q = (1̄01) : (011)......	—	—	—	45 4	
qn = (011) : (121)......	—	—	—	26 41	
np = (121) : (110)......	—	—	—	36 55	
qp = (011) : (110)......	40	63 16– 63 47	63 34	63 36	2
ps′ = (110) : (101̄)......	—	—	—	71 30	
pq = (110) : (01̄1)......	40	116 10–116 42	116 26	116 24	2
r′o′ = (2̄01) : (1̄11)......	7	34 37– 34 46	34 40	34 45	5
o′p = (1̄11) : (110)......	6	92 35– 92 53	92 43	92 42	1
pr′ = (110) : (201̄)......	30	52 24– 52 49	52 37	52 33	4
r′p = (2̄01) : (110)......	34	127 10–127 34	127 28	127 27	4
Total (11 crystals) ...	490				

Molecular Volume.—$\dfrac{M}{d} = \dfrac{615\cdot92}{2\cdot763} = 222\cdot92.$

Molecular Distance Ratios (topic axial ratios).—

$$\chi : \psi : \omega = 6\cdot3333 : 8\cdot5332 : 4\cdot2734.$$

Orientation of Optical Ellipsoid.—Plane of optic axes $b\{010\}$. Sign of double refraction, positive. The first median line is the γ axis of the indicatrix, and the second median line is α.

Extinction Direction (Axis α) in Symmetry Plane.

Plate I......1° 51′,　　Plate II......2° 12′,　　Mean......2° 2′,
behind the normal to c (001), towards the vertical axis c.

As that normal is 15° 9′ in front of the vertical axis, the second median line, the extinction direction in question, is 13° 7′ in front of the vertical axis c. The first median line lies 2° 2′ above the axis a. Both median lines thus lie in the obtuse axial angle ac. Fig. 3 will render the conditions clear.
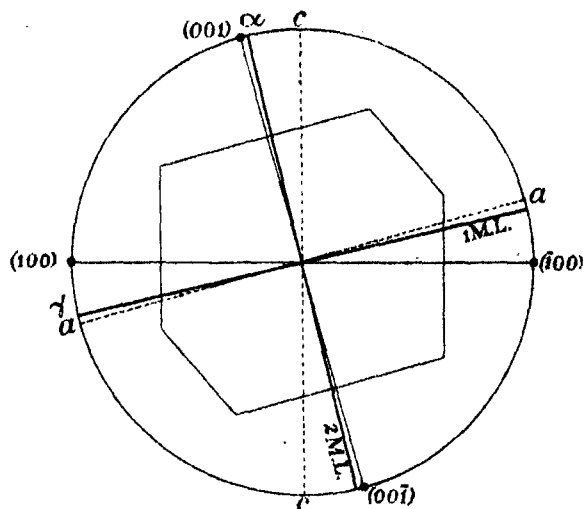
Fig. 3.

Optic Axial Angle.—Results with three pairs of section-plates perpendicular to the two median lines.

Apparent Optic Axial Angle in Air, 2E, of RbMn Selenate.

Light.	Plate I.	Plate II.	Plate III.	Mean 2E.
Li...................	112 1	112 12	112 20	112 11
C	112 2	112 13	112 22	112 12
Na	112 14	112 24	112 35	112 24
Tl	112 23	112 36	112 47	112 35
Cd	112 32	112 44	112 54	112 43

Determination of True Optic Axial Angle in Bromonaphthalene.

Light.	No. of plate perp. 1 M.L.	Observed 2H$_a$.	No. of plate perp. 2 M.L.	Observed 2H$_o$.	Calculated 2V$_a$.	Mean 2V$_a$.
Li........	1	59 46	1a	99 36	66 14 ⎫	
	2	59 18	2a	99 46	65 48 ⎬	66 5
	3	59 44	3a	99 38	66 12 ⎭	
C	1	59 44	1a	99 32	66 14 ⎫	
	2	59 16	2a	99 43	65 48 ⎬	66 5
	3	59 42	3a	99 34	66 12 ⎭	
Na	1	59 33	1a	99 12	66 13 ⎫	
	2 ...:......	59 4	2a	99 25	65 45 ⎬	66 2
	3	59 26	3a	99 11	66 8 ⎭	
Tl........	1	59 16	1a	98 40	66 12 ⎫	
	2	58 46	2a	98 51	65 43 ⎬	66 0
	3	59 10	3a	98 50	66 4 ⎭	
Cd	1	59 4	1a	98 23	66 9 ⎫	
	2	58 36	2a	98 32	65 42 ⎬	65 57
	3	58 56	3a	98 28	66 0 ⎭	
F	1	58 46	1a	98 3	66 2 ⎫	
	2	58 25	2a	98 14	65 41 ⎬	65 52
	3	58 38	3a	98 11	65 52 ⎭	

Dispersion of the Median Lines.—This is very small, measurements in monochlorobenzene (of similar refractive index) having indicated that the first median line lies nearer to the inclined axis a by 8 minutes for red C hydrogen light than for green cadmium light.

Effect of Temperature on Optic Axial Angle.—Determinations at a series of temperatures up to 75° C. indicated that the optic axial angle in air, 2E, diminishes by $3\frac{1}{4}$° for the 60° of rise of temperature, from 15° to 75° C.

Refractive Indices.—Determinations obtained with six 60°-prisms, each ground to afford two indices directly, afforded the following mean values.

Refractive Indices of Rubidium Manganese Selenate.

Light.	a.	β.	γ.
Li................	1·5059	1·5105	1·5220
C	1·5064	1·5110	1·5226
Na	1·5094	1·5140	1·5258
Tl................	1·5125	1·5172	1·5292
Cd	1·5143	1·5190	1·5312
F	1·5163	1·5210	1·5332
G	1·5225	1·5270	1·5396

Mean of a, β, and γ for Na light = 1·5164.

a = Vibration direction parallel to second median line, 18° 7′ in front of axis c.
β = ,, ,, ,, symmetry axis b.
γ = ,, ,, ,, first median line, 2° 2′ above axis a.

Double refraction, Na$_{\gamma-a}$ = 0·0164.

General formula for β, corrected to a vacuum :—

$$\beta = 1\cdot4978 + \frac{623\ 971}{\lambda^2} - \frac{1\ 653\ 300\ 000\ 000}{\lambda^4} + \ldots.$$

The α indices are also reproduced by the formula if the constant $1\cdot4978$ be diminished by $0\cdot0046$, and the γ indices if it be increased by $0\cdot0118$.

Observations at $65°$ indicated that the refractive indices diminish with rise of temperature, to the extent of $0\cdot0013$ for $50°$ rise of temperature.

Axial Ratios of the Optical Ellipsoid—

$\alpha : \beta : \gamma = 0\cdot9969 : 1 : 1\cdot0078,$ $\mathfrak{a} : \mathfrak{b} : \mathfrak{c} = 1\cdot0031 : 1 : 0\cdot9923.$

Molecular Optical Constants.

	Axis of optical indicatrix.		α.	β.	γ.
Lorenz	Specific refraction, $\dfrac{n^2-1}{(n^2+2)d} = \mathfrak{n}$	C G	0·1076 0·1105	0·1084 0·1113	0·1105 0·1135
	Molecular refraction, $\dfrac{n^2-1}{n^2+2}\cdot\dfrac{M}{d} = \mathfrak{m}$...	C G	66·27 68·04	66·78 68·58	68·06 69·90
	Specific dispersion, $\mathfrak{n}_G - \mathfrak{n}_C$		0·0029	0·0029	0·0080
	Molecular dispersion, $\mathfrak{m}_G - \mathfrak{m}_C$		1·77	1·75	1·84
Gladstone ...	Molecular refraction, $\dfrac{n-1}{d}M$ C		112·88	113·91	116·50

Mean molecular refraction (Gladstone), $\frac{1}{3}(\alpha + \beta + \gamma) = 114\cdot43.$

Cæsium Manganese Selenate, $Cs_2Mn(SeO_4)_2 \cdot 6H_2O.$

Crystal System.—Monoclinic.   Class No. 5, holohedral-prismatic.

Axial Angle.—$\beta = 106° 22'.$

Ratio of Axes.—$a : b : c = 0\cdot7319 : 1 : 0\cdot4957.$

Forms observed.—$a\{100\},\ b\{010\},\ c\{001\},\ p\{110\},\ p'\{120\},\ p'''\{130\},$ $q\{011\},\ r'\{\bar{2}01\},\ o'\{\bar{1}11\}.$

Habit.—That characteristic of the cæsium salts of the series, namely, more or less narrow $c\{001\}$ faces, broader $q\{011\}$ faces, and only moderately prominent $p\{110\}$ faces, scarcely ever tall enough to impart prismatic habit parallel to the vertical axis, although the crystals are often prismatic parallel to the inclined axis a.   Fig. 4 represents a typical crystal.
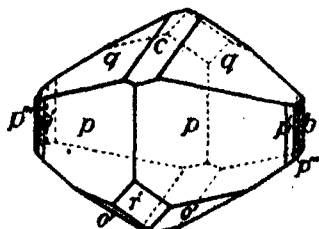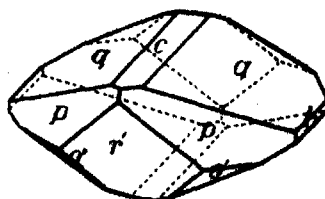
FIG. 4.   FIG. 5.

Typical crystals of cæsium manganese selenate.

The $r'\{\bar{2}01\}$ faces were almost always better developed than usual, and sometimes were as relatively large as shown in fig. 5. Faces of the subsidiary prisms $p'\{120\}$, and $p'''\{130\}$, were nearly always present, and the hemipyramid $o'\{\bar{1}11\}$ faces were also ubiquitous and often quite well developed. The clinopinakoid $b\{010\}$ was sometimes present as a fairly broad strip, but usually was very narrow or absent. The orthopinakoid $a\{100\}$ was only found as a very narrow strip, practically a line. A table of angles is given on the next page.

The crystals of this salt are particularly brilliant and transparent, and exhibit a faint pink colour.

Cleavage.—That common to the series, parallel $r'\{\bar{2}01\}$, perfect.

Relative Density.—Six determinations were carried out by the immersion method on crystals small and perfectly clear.

I.	Density for	18° ·2/4°	......	3 ·0086	For 20°/4°	3 ·0081
II.	„	17° ·6/4°	......	3 ·0087	„	3 ·0080
III.	„	15° ·5/4°	......	3 ·0129	„	3 ·0115
IV.	„	17° ·6/4°	......	3 ·0105	„	3 ·0098
V.	„	17° ·4/4°	......	3 ·0094	„	3 ·0086
VI.	„	17° ·6/4°	......	3 ·0094	„	3 ·0087

Mean ...... 3 ·0088

Accepted value for 20°/4°......**3·008**.

Molecular Volume.—$\dfrac{M}{d} = \dfrac{709·92}{3·008} = 236·01.$

Molecular Distance (topic axial) *ratios.*—

$$\chi : \psi : \omega = 6·4297 : 8·7850 : 4·3547.$$

Orientation of Optical Ellipsoid.—Plane of optic axes $b\{010\}$. Sign of double refraction positive. The first median line is the γ axis of the indicatrix, and the second line median is α.

Extinction Direction (2 M.L.) in Symmetry Plane.

Plate I......5° 52',   Plate II......5° 45',

Mean extinction angle......... 5° 49',

in front of the normal to $c\{001\}$ and away from the vertical axis c. As that normal is 16° 22' in front of the vertical axis, this extinction direction, which is that of the second median line, is situated 22° 11' in front of the vertical axis c. The first median line is 5° 49' below the axis a. These dispositions will be clear from fig. 6.

Interfacial Angles of Cæsium Manganese Selenate.

Angle.	No. of measurements.	Limits.	Mean observed.	Calculated.	Diff.
ac = (100) : (001)	4	78 29– 78 42	78 35	73 38	3
as = (100) : (101)	—	—	—	44 59	
sc = (101) : (001)	—	—	—	28 89	
cr' = (001) : (201)	17	64 26– 64 48	64 35	64 35	0
cs' = (001) : (101)	—	—	—	38 48	
$s'r'$ = (101) : (201)	—	—	—	25 47	
$r'a$ = (201) : (100)	8	41 25– 42 5	41 50	41 47	3
$r'c$ = (201) : (001)	17	115 16–115 34	115 25	115 25	0
ap = (100) : (110)	2	34 56– 35 4	35 0	35 4	4
ap'' = (100) : (210)	—	—	—	19 20	
$p''p$ = (210) : (110)	—	—	—	15 44	
pp' = (110) : (120)	14	19 10– 19 48	19 27	19 28	1
$p'p'''$ = (120) : (130)	2	9 45 - 10 14	10 0	10 3	3
$p'b$ = (120) : (010)	7	85 20– 35 45	35 35	35 28	7
pp''' = (110) : (130)	4	29 16– 30 2	29 31	29 31	0
$p'''b$ = (130) : (010)	4	25 25– 25 35	25 30	25 25	5
pb = (110) : (010)	17	54 42– 55 17	54 57	54 56	1
pp = (110) : (110)	21	70 0– 70 19	70 7	*	
pp = (110) : (110)	22	109 32–109 59	109 51	109 53	2
cq = (001) : (011)	39	25 18– 25 37	25 26	*	
qb = (011) : (010)	16	64 27– 64 30	64 34	64 34	0
qq = (011) : (011)	18	128 55–129 14	129 7	129 8	1
ao = (100) : (111)	—	—	—	48 7	
oq = (111) : (011)	—	—	—	27 8	
aq = (100) : (011)	—	—	—	75 15	
qo' = (011) : (111)	—	—	—	35 3	
$o'a$ = (111) : (100)	—	—	—	69 42	
ro = (001) : (111)	—	—	—	34 5	
op = (111) : (110)	—	—	—	42 35	
cp = (001) : (110)	38	76 22– 76 49	76 40	*	
po' = (110) : (111)	31	58 15– 58 48	58 26	58 27	1
$o'o$ = (111) : (001)	32	44 32– 45 13	44 53	44 53	0
pc = (110) : (001)	38	103 8–103 38	103 20	103 20	0
bn = (010) : (121)	—	—	—	54 58	
no = (121) : (111)	—	—	—	15 43	
bo = (010) : (111)	—	—	—	70 41	
os = (111) : (101)	—	—	—	19 19	
bo' = (010) : (111)	24	65 19– 65 31	65 26	65 23	3
os' = (111) : (101)	—	—	—	24 37	
$o'o'$ = (111) : (111)	9	49 5– 49 19	49 12	49 14	2
sq = (101) : (011)	—	—	—	37 35	
qp = (011) : (110)	40	87 36– 88 8	87 50	87 48	2
ps = (110) : (101)	—	—	—	54 37	
pq = (110) : (011)	40	91 57– 92 28	92 11	92 12	1
$s'q$ = (101) : (011)	—	—	—	45 16	
qn = (011) : (121)	—	—	—	26 26	
np = (121) : (110)	—	—	—	36 30	
qp = (011) : (110)	42	62 46– 63 2	62 55	62 56	1
ps' = (110) : (101)	—	—	—	71 48	
pq = (110) : (011)	41	116 58–117 14	117 5	117 4	1
$r'o'$ = (201) : (111)	30	34 49– 35 15	35 1	35 3	2
$o'p$ = (111) : (110)	30	92 20– 92 48	92 35	92 34	1
pr' = (110) : (201)	32	52 17– 52 40	52 24	52 23	1
$r'p$ = (201) : (110)	32	127 15–127 42	127 36	127 37	1
Total (11 crystals) ...	671				

Fig. 6.

Optic Axial Angle.—Results with three pairs of plates ground perpendicular to the first and second median lines.

Apparent Optic Axial Angle in Air, 2E, of CsMn Selenate.

Light.	Plate 1.	Plate 2.	Plate 3.	Mean 2E.
Li	121 27	119 46	121 30	120 54
C	121 23	119 42	121 26	120 50
Na	120 48	119 18	121 0	120 22
Tl	120 29	119 8	120 42	120 5
Cd	120 8	118 50	120 13	119 44

Determination of True Optic Axial Angle in Bromonaphthalene.

Light.	No. of plate perp. 1 M.L.	Observed $2H_a$.	No. of plate perp. 2 M.L.	Observed $2H_o$.	Calculated $2V_a$.	Mean $2V_a$.
Li	1	62 56	1a	98 51	69 5	
	2	62 56	2a	98 54	68 59 }	69 3
	3	63 5	3a	99 4	69 2	
C	1	62 51	1a	98 29	69 5	
	2	62 52	2a	98 50	68 57 }	69 1
	3	63 1	3a	99 1	69 0	
Na	1	62 30	1a	98 16	68 54	
	2	62 28	2a	98 21	68 50 }	68 49
	3	62 32	3a	98 45	68 44	
Tl	1	61 56	1a	98 4	68 32	
	2	61 59	2a	97 56	68 38 }	68 33
	3	62 3	3a	98 30	68 28	
Cd	1	61 28	1a	97 56	68 14	
	2	61 31	2a	97 48	68 20 }	68 17
	3	61 46	3a	98 24	68 17	
F	1	61 7	1a	97 45	68 2	
	2	61 11	2a	97 30	68 11 }	68 5
	3	61 22	3a	98 14	68 2	

Dispersion of the Median Lines.—The first median line is dispersed so that for cadmium green light it is 10 minutes nearer to the axis *a* than for red C-light. The determination was made during immersion of the section plate 1, 2, or 3 in methyl salicylate, the refraction of which is almost exactly the same as the mean refraction of the crystal.

Effect of Temperature on Optic Axial Angle.—On heating one of the section-plates gradually to 70° C., the optic axial angle in air 2E diminished to 115° 5′ for sodium light, a diminution of 5° for 55° of rise of temperature.

Refractive Indices.—Results with six 60°-prisms, each ground to afford two indices directly—

Refractive Indices of Cæsium Manganese Selenate.

Light.	α.	β.	γ.
Li	1·5215	1·5243	1·5301
C	1·5220	1·5248	1·5306
Na	1·5250	1·5279	1·5338
Tl	1·5283	1·5312	1·5373
Cd	1·5302	1·5331	1·5394
F	1·5323	1·5350	1·5415
G	1·5379	1·5405	1·5471

Mean of α, β, and γ for Na light = 1·5289.

α = Vibration direction parallel to second median line, 22° 11′ in front of axis *c*.

β = ,, ,, ,, symmetry axis *b*.

γ = ,, ,, ,, first median line, 5° 49′ below axis *a*.

Double refraction, $Na_{\gamma-\alpha}$ = 0·0088.

General formula for the intermediate refractive index β, corrected to a vacuum (correction + 0·0004) :—

$$\dot\beta = 1\cdot5112 + \frac{641\ 068}{\lambda^2} - \frac{1\ 646\ 000\ 000\ 000}{\lambda^4} + \dots$$

The α indices are also reproduced very closely by the formula if the constant 1·5112 be diminished by 0·0029 and the γ indices if the constant be increased by 0·0059.

Observations at 65° C. showed that the refractive indices are diminished by about 0·0013 (varying from 0·0011 for α to 0·0016 for γ) for 50° rise of temperature.

Axial Ratios of the Optical Ellipsoid—

α : β : γ = 0·9981 : 1 : 1·0039,   a : b : c = 1·0019 : 1 : 0·9961.

Molecular Optical Constants.

	Axis of optical indicatrix.		α.	β.	γ.
Lorenz	Specific refraction, $\dfrac{n^2-1}{(n^2+2)d} = n$	$\begin{cases} C \\ G \end{cases}$	0·1014 0·1040	0·1018 0·1044	0·1028 0·1054
.	Molecular refraction, $\dfrac{n^2-1}{n^2+2} \cdot \dfrac{M}{d} = m$ ...	$\begin{cases} C \\ G \end{cases}$	71·98 73·81	72·30 74·10	72·97 74·86
	Specific dispersion, $n_\theta - n_c$		0·0026	0·0026	0·0026
	Molecular dispersion, $m_\theta - m_c$		1·83	1·80	1·89
Gladstone ...	Molecular refraction, $\dfrac{n-1}{d} M$ C		123·20	123·86	125·23

Mean molecular refraction (Gladstone), $\frac{1}{3}(\alpha+\beta+\gamma) = 124·10$.

Ammonium Manganese Selenate $(NH_4)_2Mn(SeO_4)_2 . 6H_2O$.

Crystal System.—Monoclinic.   Class No. 5, holohedral-prismatic.

Axial Angle.—$\beta = 106° 16'$.   The value found by Topsøe was $106° 14'$.

Ratio of Axes.—$a : b : c = 0·7427 : 1 : 0·4994$.

Topsøe's values $0·7416 : 1 : 0·4979$.

Forms observed.—$a\{100\}$, $b\{010\}$, $c\{001\}$, $p\{110\}$, $p'\{120\}$, $p''\{210\}$, $p'''\{130\}$, $q\{011\}$, $o'\{\bar{1}11\}$, $r'\{\bar{2}01\}$, $n'\{\bar{1}21\}$.

The forms a and p'' were not observed by Topsøe.

Habit.—A great variety of habit is exhibited by this salt, but figs. 7 and 8 are typical illustrations.   A more or less tabular form, parallel to a pair of
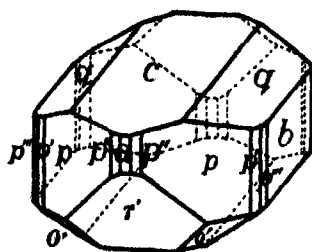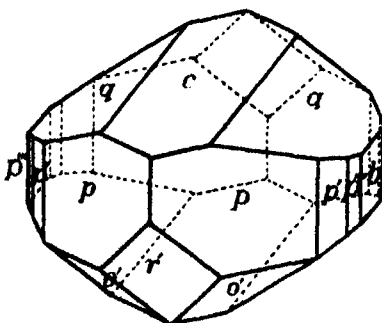
FIG. 7.   FIG. 8.

Typical crystals of ammonium manganese selenate.

either $c\{001\}$, $p\{110\}$, or $r'\{\bar{2}01\}$ faces (see fig. 3, p. 250, illustrating ammonium cadmium selenate), is common.   Occasionally a prismatic habit parallel to the vertical axis is observed, like fig. 7 but more elongated vertically.   The $q\{011\}$ faces show every variety of relative size, from small (characteristic of the potassium salts of the series) to about as large as the c faces (characteristic of the rubidium salts), as shown in figs. 7 and 8.   Very often no faces are apparent but those of $c\{001\}$, $q\{011\}$, $p\{110\}$, and $r'\{\bar{2}01\}$.   The subordinate

prism-faces $p'\{120\}$, $p'''\{130\}$, and $p''\{210\}$ were usually mere lines, but in certain crops of larger crystals quite large faces of $p'\{120\}$ and $p'''\{130\}$ were present, as shown in fig. 8. The faces of the hemi-pyramid $o'\{\bar{1}11\}$ were often fairly considerably developed when present at all, but the rarer form $n'\{\bar{1}21\}$ was never developed sufficiently to afford measurements more than merely adequate for identification. The results of the measurements are given on the next page.

The crystals were beautifully clear and transparent and exhibited a faint pink colour.

Cleavage.—The usual cleavage parallel to $r'\{\bar{2}01\}$ common to the series is exhibited, and also an even more perfect one parallel to $b\{010\}$.

Relative Density.—Six determinations were made by the immersion method, with excellent small crystals.

				For 20°/4°		
I.	Density for 18° ·9/4°	......	2 ·1606	For 20°/4°	......	2 ·1604
II.	„	18' ·2/4°	...... 2 ·1551	„	......	2 ·1547
III.	„	19° ·1/4°	...... 2 ·1614	„	......	2 ·1612
IV.	„	19° ·1/4°	...... 2 ·1562	„	......	2 ·1560
V.	„	19° ·8/4°	...... 2 ·1598	„	......	2 ·1598
VI.	„	19° ·5/4°	...... 2 ·1578	„	......	2 ·1577
				Mean	......	2 ·1583

Accepted value for 20°/4°......**2·158**.

Molecular Volume.—$\dfrac{M}{d} = \dfrac{481\cdot98}{2\cdot158} = 223\cdot35$.

Topsøe obtained the lower value 2·093 for the specific gravity, and consequently also a molecular volume too high, namely, 232·2.

Molecular Distance (topic axial) ratios.—

$$\chi : \psi : \omega = 6\cdot3577 : 8\cdot5603 : 4\cdot2750.$$

Orientation of Optical Ellipsoid.—Plane of optic axes $b\{010\}$. Sign of double refraction, positive. The first median line is the γ axis of the indicatrix, and α is the second median line.

Extinction Direction (2M.L.) in Symmetry Plane.

Plate I...13° 12', Plate II...13° 20', Plate III...12° 10', Mean...12° 54', behind the normal to $c\{001\}$. As the normal to $c\{001\}$ lies 16° 16' in front of the vertical axis c, this extinction direction, which is the second median line, lies 3° 22' in front of the vertical axis. The first median line lies 12° 54' above the axis a. Both median lines thus lie in the obtuse axial angle ac. Fig. 9 will render the conditions clear.

Interfacial Angles of Ammonium Manganese Selenate.

Angle.	No. of measurements.	Limits.	Mean observed.	Calculated.	Diff.	Topsøe's values.
$ac = (100):(001)$...	8	73 30– 73 58	73 44	73 44	0	73 46
$as = (100):(101)$...	—	—	—	45 14	—	
$sc = (101):(001)$...	—	—	—	28 30	—	
$cr' = (001):(\bar{2}01)$...	20	63 58– 64 25	64 10	64 12	2	64 8
$cs' = (001):(\bar{1}01)$...	—	—	—	38 28	—	
$s'r' = (\bar{1}01):(\bar{2}01)$...	—	—	—	25 44	—	
$r'a = (\bar{2}01):(100)$...	2	41 54– 42 16	42 5	42 4	1	
$r'c = (\bar{2}01):(00\bar{1})$...	20	115 35–116 3	115 50	115 48	2	115 52
$ap = (100):(110)$...	6	35 23– 35 34	35 27	35 29	2	
$ap'' = (100):(210)$...	1	—	19 40	19 37	3	
$p''p = (210):(110)$...	1	—	15 54	15 52	2	
$pp' = (110):(120)$...	1	—	19 25	19 28	3	19 28
$p'b = (120):(010)$...	1	—	35 6	35 3	3	35 5
$pp''' = (110):(130)$...	3	29 12– 29 32	29 21	29 27	6	29 28
$p'''b = (130):(010)$...	2	24 59– 25 1	25 0	25 4	4	25 5
$p'p''' = (120):(130)$...	—	—	—	9 59	—	10 0
$pb = (110):(010)$...	27	54 8– 54 46	54 31	54 31	0	54 33
$pp = (110):(\bar{1}10)$...	22	70 42– 71 15	70 58	*	—	70 54
$pp = (110):(\bar{1}10)$...	20	108 41–109 28	109 3	109 2	1	109 6
$cq = (001):(011)$...	42	25 22– 25 50	25 37	*	—	25 33
$qb = (011):(010)$...	31	64 12– 64 38	64 24	64 23	1	64 27
$qq = (011):(01\bar{1})$...	20	128 24–129 13	128 47	128 46	1	128 54
$ao = (100):(111)$...	—	—	—	48 25	—	
$oq = (111):(011)$...	—	—	—	26 57	—	
$aq = (100):(011)$...	—	—	—	75 22	—	75 23
$qo' = (011):(\bar{1}11)$...	—	—	—	34 43	—	84 40
$o'a = (\bar{1}11):(100)$...	—	—	—	69 55	—	
$co = (001):(111)$...	—	—	—	34 5	—	
$op = (111):(110)$...	—	—	—	42 44	—	
$cp = (001):(110)$...	42	76 38– 77 8	76 49	*	—	76 50
$po' = (110):(11\bar{1})$...	22	58 12– 58 51	58 33	58 27	6	
$o'c = (11\bar{1}):(001)$...	22	44 21– 45 12	44 38	44 44	6	44 38
$pc = (110):(00\bar{1})$...	42	103 0–103 25	103 11	103 11	0	103 10
$bn = (010):(121)$...	—	—	—	54 39	—	
$no = (121):(111)$...	—	—	—	15 50	—	
$bo = (010):(111)$...	—	—	—	70 29	—	
$os = (111):(101)$...	—	—	—	19 31	—	
$bn' = (010):(\bar{1}21)$...	—	—	—	47 14	—	
$n'o' = (\bar{1}21):(\bar{1}11)$...	—	—	—	17 57	—	
$bo' = (010):(\bar{1}11)$...	14	65 0– 65 28	65 12	65 11	1	65 15
$o's' = (\bar{1}11):(\bar{1}01)$...	—	—	—	24 49	—	24 45
$o'o' = (\bar{1}11):(\bar{1}11)$...	8	49 35– 49 40	49 38	49 38	0	49 29
$sq = (101):(011)$...	—	—	—	37 35	—	
$qn' = (011):(\bar{1}21)$...	—	—	—	35 43	—	
$n'p = (\bar{1}21):(110)$...	—	—	—	51 41	—	
$qp = (011):(\bar{1}10)$...	34	87 18– 87 39	87 28	87 24	4	87 26
$ps = (\bar{1}10):(10\bar{1})$...	—	—	—	55 1	—	
$pq = (\bar{1}10):(0\bar{1}1)$...	34	92 22– 92 40	92 34	92 36	2	
$s'q = (\bar{1}01):(011)$...	—	—	—	45 5	—	
$qn = (011):(12\bar{1})$...	—	—	—	26 18	—	
$np = (12\bar{1}):(110)$...	—	—	—	36 32	—	
$qp = (011):(110)$...	37	62 41– 63 6	62 55	62 50	5	62 54
$ps' = (110):(10\bar{1})$...	—	—	—	72 5	—	
$pq = (110):(0\bar{1}1)$...	37	116 49–117 19	117 5	117 10	5	
$r'o' = (\bar{2}01):(\bar{1}11)$...	28	34 56– 35 43	35 11	35 9	2	35 5
$o'p = (\bar{1}11):(110)$...	20	91 47– 92 16	91 59	92 3	4	
$pr' = (110):(\bar{2}0\bar{1})$...	41	52 25– 53 9	52 49	52 48	1	52 49
$r'p = (\bar{2}01):(110)$...	41	126 50–127 30	127 11	127 12	1	127 11
Total (11 crystals)...	634					

Fig. 9.

Optic Axial Angle.—The results for 2E and for $2H_a$, $2H_o$, and the true angle $2V_a$, from three pairs of plates, ground perpendicular to the two bisectrices, are given in the next two tables.

Apparent Optic Axial Angle in Air, 2E, of AmMn Selenate.

Light.	Plate I.	Plate II.	Plate III.	Mean 2E.
Li......................	118 33	119 36	123 57	120 42
C	118 39	119 41	124 2	120 47
Na	119 54	121 4	124 32	121 50
Tl......................	120 45	122 28	125 41	122 58
Cd	121 25	123 10	126 25	123 40

Determination of True Optic Axial Angle in Bromonaphthalene.

Light.	No. of plate perp. 1 M.L.	Observed $2H_a$.	No. of plate perp. 2 M.L.	Observed $2H_o$.	Calculated $2V_a$.	Mean $2V_a$.
Li........	1	63 36	1a	97 10	70 11	70 17
	2	63 35	2a	97 11	70 10	
	3	63 54	3a	96 52	70 32	
C	1	63 35	1a	97 6	70 12	70 18
	2	63 34	2a	97 9	70 10	
	3	63 53	3a	96 49	70 33	
Na	1	63 27	1a	96 30	70 21	70 23
	2	63 27	2a	96 51	70 12	
	3	63 42	3a	96 26	70 35	
Tl........	1	63 18	1a	96 0	70 28	70 28
	2	63 8	2a	96 11	70 15	
	3	63 31	3a	95 51	70 40	
Cd	1	63 10	1a	95 34	70 32	70 31
	2	62 56	2a	95 40	70 18	
	3	63 24	3a	95 37	70 42	
F	1	63 0	1a	95 0	70 39	70 34
	2	62 40	2a	95 10	70 20	
	3	63 14	3a	95 16	70 43	

Dispersion of the Median Lines.—This was determined by immersion in monochlorobenzene, the refractive index for which is close to the mean index for the crystals. It was found to be so small, less than 5 minutes, that it was not possible to be certain of its sign, different plates showing the first median line to be nearer to axis *a* for red and blue respectively.

Effect of Temperature on Optic Axial Angle.—The angle in air 2E decreased 6° 40′ to 115° 10′ for sodium light, on raising the temperature of the section-plate gradually from the ordinary temperature (15°) to 75° C.

Refractive Indices.—Results with six 60°-prisms, each ground to afford two indices directly—

Refractive Indices of Ammonium Manganese Selenate.

Light.	*a.*	*β.*	*γ.*
Li...............	1·5124	1·5163	1·5249
C	1·5129	1·5169	1·5255
Na	1·5160	1·5202	1·5288
Tl...............	1·5194	1·5237	1·5323
Cd	1·5214	1·5256	1·5343
F	1·5235	1·5276	1·5364
G	1·5294	1·5340	1·5429

Mean of *α*, *β*, and *γ* for Na light = 1·5217.

α = Vibration direction parallel to second median line, 3° 22′ in front of vertical axis *c*.
β = ,, ,, ,, symmetry axis *b*.
γ = ,, ,, ,, first median line, 12° 54′ above inclined axis *a*.
Double refraction, Na$_{γ-α}$ = 0·0128.

General formula for *β*, corrected to a vacuum :—

$$\beta = 1\cdot5023 + \frac{690\ 197}{\lambda^2} - \frac{1\ 906\ 400\ 000\ 000}{\lambda^4} + \ldots.$$

The *α* indices are equally well reproduced by the formula if the constant 1·5023 be diminished by 0·0042, and the *γ* indices if it be increased by 0·0086.

Observations at 65° indicated that the refractive indices of ammonium manganese selenate diminish by about 0·0010 for a rise of temperature of 50°.

Axial Ratios of the Optical Ellipsoid.—

$$\alpha : \beta : \gamma = 0\cdot9972 : 1 : 1\cdot0057, \qquad \mathfrak{a} : \mathfrak{b} : \mathfrak{c} = 1\cdot0028 : 1 : 0\cdot9944.$$

Molecular Optical Constants.

	Axis of optical indicatrix.		*α.*	*β.*	*γ.*
Lorenz	Specific refraction, $\frac{n^2-1}{(n^2+2)\,d} = n$	C	0·1393	0·1402	0·1422
		G	0·1430	0·1440	0·1460
	Molecular refraction, $\frac{n^2-1}{n^2+2} \cdot \frac{M}{d} = m$ ...	C	67·12	67·56	68·51
		G	68·93	69·43	70·39
	Specific dispersion, nᴳ − nᶜ		0·0087	0·0038	0·0038
	Molecular dispersion, mᴳ − mᶜ		1·81	1·87	1·88
Gladstone ...	Molecular refraction, $\frac{n-1}{d} M$	C	114·55	115·45	117·37

Mean molecular refraction (Gladstone), $\frac{1}{3}$ (α + β + γ) = 115·79.

Comparison of Results.

Habit.—The crystals of the rubidium and cæsium salts exhibit the habits which are respectively characteristic of rubidium and cæsium salts throughout the whole series of double sulphates and selenates.

Crystal Elements and Angles.—

Comparison of the Interfacial Angles.

Angle.		RbMn selenate.	CsMn selenate.	AmMn selenate.
ac	= (100) : (001)	74 51	73 38	73 44
as	= (100) : (101)	45 52	44 59	45 14
sc	= (101) : (001)	28 59	28 39	28 30
cv'	= (001) : (201)	68 35	64 35	64 12
cs'	= (001) : (101)	38 20	38 48	38 28
s'r'	= (101) : (201)	25 15	25 47	25 44
r'a	= (201) : (100)	41 34	41 47	42 4
ap	= (100) : (110)	35 38	35 4	35 29
ap''	= (100) : (210)	19 43	19 20	19 37
p''p	= (210) : (110)	15 55	15 44	15 52
pp'	= (110) : (120)	19 28	19 28	19 28
p'b	= (120) : (010)	34 54	35 28	35 3
pp'''	= (110) : (130)	29 25	29 31	29 27
p'''b	= (130) : (010)	24 57	25 25	25 4
p'p'''	= (120) : (130)	9 57	10 3	9 59
pb	= (110) : (010)	54 22	54 56	54 31
cq	= (001) : (011)	25 48	25 26	25 37
qb	= (011) : (010)	64 12	64 34	64 28
ao	= (100) : (111)	49 4	48 7	48 25
oq	= (111) : (011)	27 19	27 8	26 57
aq	= (100) : (011)	76 23	75 15	75 22
qo'	= (011) : (111)	34 33	35 8	34 43
o'a	= (111) : (100)	69 4	69 42	69 55
co	= (001) : (111)	34 35	34 5	34 5
op	= (111) : (110)	43 9	42 35	42 44
cp	= (001) : (110)	77 44	76 40	76 49
po'	= (110) : (111)	57 44	58 27	58 27
o'c	= (111) : (001)	44 32	44 58	44 44
bn	= (010) : (121)	54 18	54 58	54 39
no	= (121) : (111)	15 56	15 48	15 50
bo	= (010) : (111)	70 14	70 41	70 29
os	= (111) : (101)	19 46	19 19	19 31
bo'	= (010) : (111)	65 17	65 23	65 11
o's'	= (111) : (101)	24 48	24 37	24 49
sq	= (101) : (011)	38 2	37 35	37 35
qp	= (011) : (110)	86 26	87 48	87 24
ps	= (110) : (101)	55 32	54 37	55 1
s'q	= (101) : (011)	45 4	45 16	45 5
qn	= (011) : (121)	26 41	26 26	26 18
np	= (121) : (110)	36 55	36 30	36 32
qp	= (011) : (110)	63 36	62 56	62 50
ps'	= (110) : (101)	71 20	71 48	72 5
r'o'	= (201) : (111)	34 45	35 8	35 9
o'p	= (111) : (110)	92 42	92 34	92 3
pr'	= (110) : (201)	52 33	52 23	52 48

The interfacial angles of the rubidium and cæsium salts bear the same relations to each other as do the angles of the rubidium and cæsium salts of all the other groups of the series investigated, the signs of the differences being the same. The axial ratios are also similarly related. The angles and ratios of the ammonium salt are adequately close for true isomorphism, but are not eutropically related to the metallic salt-values. The values of the great majority of the angles are intermediate between the values for the two metallic salts.

Comparison of the Axial Angles and Axial Ratios.

	Axial angles.	Axial ratios.
	β.	a : b : c
Rubidium manganese selenate ....,.........	105° 9′	0·7422 : 1 : 0·5008
Ammonium ,, ,, ...	106° 16′	0·7427 : 1 : 0·4994
Cæsium ,, ,, ...	106° 22′	0·7319 : 1 : 0·4957

Volume Constants.—

Volume Constants of the Manganese Group of Double Selenates.

Salt.	Molecular weight	Specific gravity.	Molecular volume.	Topic axial ratios.
				χ : ψ : ω
RbMn selenate	615·92	2·763	222·92	6·3333 : 8·5332 : 4·2734
CsMn ,, ...	709·92	3·008	236·01	6·4297 : 8·7850 : 4·3547
NH₄Mn ,, ...	481·98	2·158	223·35	6·3577 : 8·5603 : 4·2750

The usual progression observed in the series, with the atomic number of the alkali metal, is apparent in molecular volume and topic axial ratios on passing from the rubidium to the cæsium salt; and the ammonium salt is, as usual, practically isostructural with the rubidium salt, the molecular volumes and topic axial ratios (relative dimensions of the elementary cells of the space-lattices) being nearly identical.

There is an increase of molecular volume of 13·09 units on replacing rubidium by cæsium, an amount of the same order as was observed in the iron group (12·92) of double selenates, and in the manganese (12·69) and iron (12·96) groups of double sulphates.

Cleavage.—There is a perfect cleavage parallel to the orthopinakoid r' {$\bar{2}01$} in the crystals of all three salts. This is the common cleavage direction of the whole series of double sulphates and selenates. In addition, however, ammonium manganous selenate cleaves with facility along the symmetry plane b {010}.

Orientation of Optical Ellipsoid.—The position of the ellipsoid is conveniently determined by giving the position, for a specific wave-length, of that

one of its two rectangular axes lying in the symmetry plane which is not far removed from the vertical crystal axis c; it is the α axis of the indicatrix and the second median line for all the salts.

Inclination of α Axis of Indicatrix to Vertical Axis c, in front, for Na Light.

NH₄Mn selenate	....	3° 32′
RbMn	„	....	13° 7′
CsMn	„	....	22° 11′

It will be observed that the position of this axis for the ammonium salt is nearest the vertical axis c, and that the optical ellipsoid rotates further and further away from this position, in the symmetry plane, for the rubidium and cæsium salts, as in all the other groups of the series previously studied. Fig. 10 gives a comparative view of the positions of the axes of the indicatrix lying in the symmetry plane for all three salts, and will render the meaning of this table of inclinations clear.
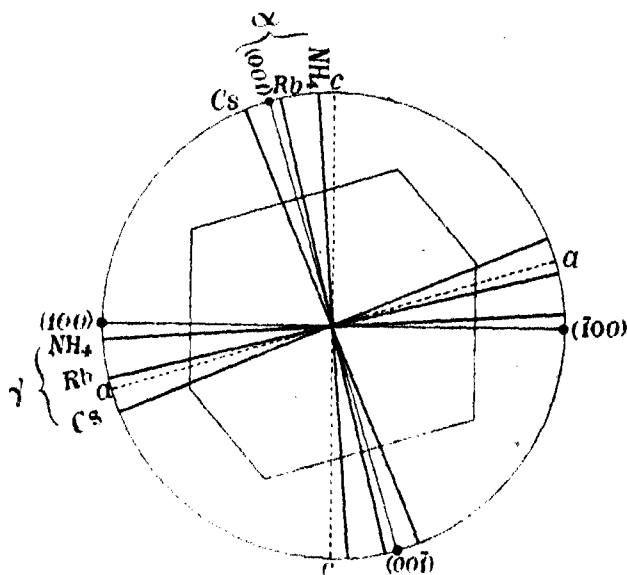
FIG. 10.

Optic Axial Angles.—The plane of symmetry $b\{010\}$ is the common plane of the optic axes for the whole group. The optic axial angles are as follows.

In the absence of a potassium salt a complete comparison is not possible, but the relations are similar to those in other groups.

Optic Axial Angles $2V_a$ of the Manganese Group of Double Selenates.

	AmMn selenate.	RbMn selenate.	CsMn selenate.
Li	70 17	66 5	69 3
C	70 18	66 5	69 1
Na	70 23	66 2	68 49
Tl	70 28	66 0	68 33
Cd	70 31	65 57	68 17
F	70 34	65 52	68 5

Refractive Indices.—The refractive indices are compared in the accompanying Table. Both the refractive index and the double refraction change progressively, the former increasing and the latter decreasing with the atomic number of the alkali metal, and the indices of the ammonium salt are intermediate between those for the two alkali metallic salts.

Comparison of the Refractive Indices.

Index.	Light.	RbMn selenate.	NH₄Mn selenate.	CsMn selenate.
	Li	1·5059	1·5124	1·5215
	C	1·5064	1·5129	1·5220
	Na	1·5094	1·5160	1·5250
a	Tl	1·5125	1·5194	1·5283
	Cd	1·5143	1·5214	1·5302
	F	1·5163	1·5235	1·5323
	G	1·5225	1·5294	1·5379
	Li	1·5105	1·5163	1·5248
	C	1·5110	1·5169	1·5248
	Na	1·5140	1·5202	1·5279
β	Tl	1·5172	1·5237	1·5312
	Cd	1·5190	1·5256	1·5331
	F	1·5210	1·5276	1·5350
	G	1·5270	1·5340	1·5405
	Li	1·5220	1·5249	1·5301
	C	1·5226	1·5255	1·5306
	Na	1·5258	1·5288	1·5338
γ	Tl	1·5292	1·5323	1·5373
	Cd	1·5312	1·5343	1·5394
	F	1·5332	1·5364	1·5415
	G	1·5396	1·5429	1·5471
Mean refractive index $\frac{1}{3}(a + \beta + \gamma)$ for Na light		1·5164	1·5217	1·5289
Double refraction, Na$_{\gamma-a}$		0·0164	0·0128	0·0088

Axial Ratios of the Optical Indicatrix.—These are as under, and are related for the three salts just as in other groups of the series.

Axial Ratios of the Optical Indicatrix.

$$a \ : \ \beta \ : \ \gamma$$

RbMn selenate .... $0·9969 : 1 : 1·0078$

NH₄Mn ,, ... $0·9972 : 1 : 1·0057$

CsMn ,, ... $0·9981 : 1 : 1·0039$

Molecular Optical Constants.—The molecular refraction increases with the atomic number of the alkali metal, and the value for the ammonium salt is about the same as that for the rubidium salt, corresponding to the isostructure of the two salts.

Specific Refraction and Dispersion (Lorenz).

Selenate.	Specific refraction, $\frac{n^2-1}{(n^2+2)\,d} = n$.						Specific dispersion. $n_G - n_C$.		
	For ray C(Ha).			For ray Hγ near G.					
	a.	β.	γ.	a.	β.	γ.	a.	β.	γ.
AmMn ...	0·1393	0·1402	0·1422	0·1430	0·1440	0·1450	0·0037	0·0038	0·0038
RbMn ...	0·1076	0·1084	0·1105	0·1105	0·1113	0·1135	0·0029	0·0029	0·0030
CsMn......	0·1014	0·1018	0·1028	0·1040	0·1044	0·1054	0·0026	0·0026	0·0026

Molecular Refraction and Dispersion (Lorenz).

Selenate.	Molecular refraction, $\frac{n^2-1}{n^2+2} \cdot \frac{M}{d} = m$.						Molecular dispersion. $m_G - m_C$.		
	For ray C (Ha).			For ray Hγ near G.					
	a.	β.	γ.	a.	β.	γ.	a.	β.	γ.
RbMn	66·27	66·78	68·06	68·04	68·53	69·90	1·77	1·75	1·84
AmMn	67·12	67·56	68·51	68·93	69·43	70·39	1·81	1·67	1·88
CsMn	71·98	72·30	72·97	73·81	74·10	74·86	1·83	1·80	1·89

Molecular Refraction (Gladstone and Dale).

Selenate.	$\frac{n-1}{d}$ M for ray C.			Mean molecular refraction for ray C. $\frac{1}{3}(a+\beta+\gamma)$.
	a.	β.	γ.	
RbMn	112·88	113·91	116·50	114·43
AmMn	114·55	115·45	117·37	115·79
CsMn	123·20	123·86	125·23	124·10

General Conclusions.

It has thus been found that the crystals of the hexahydrated rubidium manganous and cæsium manganous selenates exhibit the same progression in all their properties—morphological (habits, interfacial angles, axial angles, and space-lattice cell-dimensions) and optical—with the progressive increase of the atomic number of the alkali metal, which has been observed throughout every group (salts containing the same M-metal) of this great series of isomorphous salts, $R_2M(\genfrac{}{}{0pt}{}{S}{Se}O_4)_2.6H_2O$.

If the potassium salt of the group could be obtained there is no doubt it would fall into line as the first member of the group, and it is even possible

to specify what its constants would be, within a very slight margin of possible error. Moreover, ammonium manganous selenate hexahydrate is almost exactly isostructural with its rubidium analogue, a fact in line with the results afforded for all analogous pairs of ammonium and rubidium salts throughout both this monoclinic series and the rhombic series of simple salts, $R_2 \underset{Se}{\overset{S}{}} O_4$.

Monoclinic Double Selenates of the Cadmium Group.

By A. E. H. TUTTON, D.Sc., M.A., F.R.S.

Like the manganese group, the cadmium group of hexahydrated double selenates consists of only three salts, those containing rubidium, cæsium, and ammonium, the potassium salt being incapable of preparation and apparently of existence. A potassium cadmium selenate with two molecules of water is obtained instead, and was described by Von Hauer in the year 1866, and by Topsøe in 1870.[*] Indeed, so near in this group is even the rubidium salt to the limit of existence that it has only been obtained at all after many and prolonged attempts. Moreover, it was only formed then in small quantity in the very coldest weather, the great majority of crystals even in these few crops having been those of the salt just referred to with other than six molecules of water. Almost as great difficulty has also been found in preparing the cæsium salt, and the crystals of both these alkali metallic salts of the hexahydrated group have always been white and opaque, so that no optical investigation has been possible. These salts, indeed, would appear never to have been previously obtained at all. Moreover, the ammonium salt, which was obtained by Von Hauer and measured by Topsøe,[*] affords crystals which are for the most part opaque, and are described by Topsøe as being porcelain-like. No optical investigation of them has ever previously been attempted; they were not included by Topsøe and Christiansen in their great work. The author has succeeded, however, in obtaining a very few crystals of ammonium cadmium selenate hexahydrate, which remained sufficiently transparent for the few hours, after their removal from the mother liquor, necessary to enable them to be subjected to a fairly complete optical investigation. The method followed was the rapid one used in the even more difficult case of potassium ferrous selenate.[†]

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[*] Haldor Topsøe, 'Krystallogr.-kem. Unders. o. de Selensure Salte,' Copenhagen, 1870.

[†] 'Phil. Trans.,' A, vol. 218, p. 401 (1919).

The cadmium selenate used in preparing the double salts was obtained by precipitating a solution of cadmium sulphate with a just adequate quantity of sodium hydrate, and dissolving the thoroughly washed precipitate in selenic acid. Equal molecular quantities of solutions of cadmium selenate and of the alkali selenate were then mixed, and the liquid at once filtered and set out for spontaneous evaporation and crystallisation, with the results just specified.

Rubidium Cadmium Selenate, $Rb_2Cd(SeO_4)_2 . 6H_2O$.

Crystal System.—Monoclinic.   Class No. 5, holohedral-prismatic.

Axial Angle.—$\beta = 105° 7'$.

Ratio of Axes.—$a : b : c = 0.7402 : 1 : 0.5026$.

Forms observed.—$b\{010\}$, $c\{001\}$, $p\{110\}$, $p'\{120\}$, $q\{011\}$, $r'\{\bar{2}01\}$, $o'\{111\}$.

Habit.—That characteristic of all the rubidium salts of the series, the faces of $q\{011\}$ being nearly as large as those of $c\{001\}$. But the faces of $r'\{\bar{2}01\}$ were generally developed to an unusually large extent, a feature which is also exhibited by the sulphur analogue, rubidium cadmium sulphate. A typical crystal is portrayed in fig. 1.
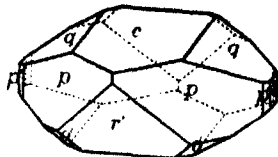
FIG. 1.—Typical crystal of rubidium cadmium selenate.

It was only after many attempts that measurable crystals were eventually obtained during nights of intense frost, and they were quite opaque, white like porcelain, even from the first. They were isolated crystals scattered here and there in the midst of a crop of transparent crystals of the di-hydrate. The angular measurements were made immediately after removal from the mother liquor, after careful drying with a fine linen cloth, and are quite trustworthy as far as are recorded in the accompanying Table ; many other less trustworthy values were obtained, but are altogether discarded, as being below the standard of the author's work. Shortly afterwards the crystals became friable and crumbled to powder.

This hexahydrated salt thus appears to be metastable at the ordinary temperature, and even down to 0° C. or thereabouts, and decomposes to a more stable salt of lower hydration with considerable rapidity.

No cleavage was definitely ascertainable, and no density determinations of any value were possible. Optical investigation was quite impossible.

Interfacial Angles of Rubidium Cadmium Selenate.

Angle.		Mean observed.	Calculated.	Diff.
ac	= (100) : (001)	—	74 53	
as	= (100) : (101)	—	45 44	
sc	= (101) : (001)	—	29 9	
cr'	= (001) : (201)	63 50	63 49	1
cs'	= (001) : (1̄01)	—	38 35	
$s'r'$	= (1̄01) : (201)	—	25 14	
$r'a$	= (201) : (1̄00)	—	41 18	
$r'c$	= (201) : (001̄)	116 10	116 11	1
ap	= (100) : (110)	—	85 33	
pp'	= (110) : (120)	—	19 28	
$p'p'''$	= (120) : (130)	—	9 58	
$p'b$	= (120) : (010)	—	34 59	
pp'''	= (110) : (130)	—	29 26	
$p'''b$	= (130) : (010)	—	25 1	
pb	= (110) : (010)	—	54 27	
pp	= (110) : (1̄10)	71 5	*	
pp	= (110) : (1̄10)	108 55	108 55	0
cq	= (001) : (011)	25 53	*	
qb	= (011) : (010)	—	64 7	
qq	= (011) : (01̄1)	128 15	128 14	1
ao	= (100) : (111)	—	48 57	
oq	= (111) : (011)	—	27 29	
aq	= (100) : (011)	—	76 26	
qo'	= (011) : (1̄11)	—	34 45	
$o'a$	= (1̄11) : (1̄00)	—	68 49	
co	= (001) : (111)	—	34 45	
op	= (111) : (110)	—	43 0	
cp	= (001) : (110)	77 45	*	
po'	= (110) : (11̄1)	—	57 29	
$o'c$	= (11̄1) : (001̄)	—	44 46	
pc	= (110) : (001̄)	102 15	102 15	0
bn	= (010) : (121)	—	54 15	
no	= (121) : (111)	—	15 57	
bo	= (010) : (111)	—	70 12	
os	= (111) : (101)	—	19 48	
bo'	= (010) : (1̄11)	—	65 15	
$o's'$	= (1̄11) : (1̄01)	—	24 45	
$o'o'$	= (1̄11) : (1̄1̄1)	—	49 30	
sq	= (101) : (011)	—	38 13	
qp	= (011) : (1̄10)	86 21	86 23	2
ps	= (1̄10) : (1̄01)	—	55 24	
pq	= (1̄10) : (01̄1)	93 39	93 37	2
$s'q$	= (1̄01) : (011)	—	45 19	
qn	= (011) : (121)	—	26 48	
np	= (121) : (110)	—	36 48	
qp	= (011) : (110)	68 35	68 36	1
ps'	= (110) : (1̄01)	—	71 5	
pq	= (110) : (01̄1)	116 25	116 24	1
$r'o'$	= (201) : (1̄11)	—	34 46	
$o'p$	= (1̄11) : (110)	—	92 55	
pr'	= (110) : (201̄)	52 25	52 19	6
$r'p$	= (201) : (110)	127 35	127 41	6

Cæsium Cadmium Selenate, $Cs_2Cd(SeO_4)_2 . 6H_2O$.

Crystal System.—Monoclinic.   Class No. 5, holohedral-prismatic.

Axial Angles.—$\beta = 106° 22'$.

Ratio of Axes.—$a : b : c = 0.7319 : 1 : 0.5011$.

Forms observed.—$a\{100\}, b\{010\}, c\{001\}, p\{110\}, p'\{120\}, q\{011\}, r'\{\bar{2}01\}$ $o'\{\bar{1}11\}$.

Habit.—That characteristic of the cæsium salts of the series, prismatic parallel to the inclined axis a, with relatively large faces of $q\{011\}$ and narrower faces of $c\{001\}$.   But, like the rubidium salt, the faces of the orthodome $r'\{\bar{2}01\}$ were also generally very prominent.   Fig. 2 represents a typical crystal.
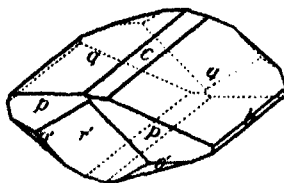
Fig. 2.—Typical crystal of cæsium cadmium selenate.

Cæsium cadmium selenate hexahydrate in general character resembles its rubidium analogue very closely to a large extent, but is distinctly less unstable, the crystals persisting longer when once formed, and often being of large size.   But they were only produced during keen frost, and amidst and often deposited upon transparent crystals of the di-hydrate, of which most of the crop was composed.

A greater number of trustworthy measurements were obtained than in the case of the rubidium salt, and are summarised in the accompanying Table.   The crystals were always opaque, however, white like porcelain, and eventually became friable.

Cleavage investigations were ambiguous and of little value, although there were indications that the usual cleavage parallel to $r'\{\bar{2}01\}$ is developed.

Density determinations were valueless, and optical investigation an impossibility.

Interfacial Angles of Cæsium Cadmium Selenate.

Angle.			Mean observed.	Calculated.	Diff.
			° ′	° ′	′
ac	= (100) : (001)	....	—	78 38	
as	= (100) : (101)	....	—	45 2	
sc	= (101) : (001)	....	—	28 36	
or′	= (001) : (2̄01)	....	64 35	64 31	4
os′	= (001) : (1̄01)	....	—	38 44	
s′r′	= (1̄01) : (2̄01)	....	—	25 47	
r′a	= (2̄01) : (1̄00)	....	—	41 51	
r′c	= (2̄01) : (00̄1)	....	115 25	115 29	4
ap	= (100) : (110)	....	—	35 6	
pp′	= (110) : (120)	....	19 25	19 28	3
p′p‴	= (120) : (130)	....	—	10 4	
p′b	= (120) : (010)	....	35 20	35 26	6
pp‴	= (110) : (130)	....	—	29 32	
p‴b	= (130) : (010)	....	—	25 22	
pb	= (110) : (010)	....	54 55	54 54	1
pp	= (110) : (1̄10)	....	70 12	*	
pp	= (110) : (1̄10)	....	109 50	109 48	2
cq	= (001) : (011)	....	25 41	*	
qb	= (011) : (010)	....	—	64 19	
qq	= (011) : (01̄1)	....	128 36	128 38	0
ao	= (100) : (111)	....	—	48 14	
oq	= (111) : (011)	....	—	27 3	
aq	= (100) : (011)	....	—	75 17	
qo′	= (011) : (1̄11)	....	—	35 16	
o′a	= (1̄11) : (1̄00)	....	—	69 27	
co	= (001) : (111)	....	—	34 9	
op	= (111) : (110)	....	—	42 31	
cp	= (001) : (110)	....	76 40	*	
po′	= (110) : (11̄1)	....	58 0	58 5	5
o′c	= (11̄1) : (001̄)	....	45 20	45 15	5
pc	= (110) : (001̄)	....	108 20	103 20	0
bn	= (010) : (121)	....	—	54 40	
no	= (121) : (111)	....	—	15 49	
bo	= (010) : (111)	....	—	70 29	
os	= (111) : (101)	....	—	19 31	
bo′	= (010) : (1̄11)	....	—	65 12	
o′s′	= (1̄11) : (1̄01)	....	—	24 48	
o′o′	= (1̄11) : (1̄1̄1)	....	—	49 36	
sq	= (101) : (011)	....	—	37 42	
qp	= (011) : (1̄10)	....	87 42	87 37	5
ps	= (1̄10) : (1̄01)	....	—	54 41	
pq	= (1̄10) : (01̄1)	....	92 18	92 23	5
s′q	= (1̄01) : (011)	....	—	45 20	
qn	= (011) : (121)	....	—	26 20	
np	= (121) : (110)	....	—	36 28	
qp	= (011) : (110)	....	62 54	62 48	6
ps′	= (110) : (101̄)	....	—	71 52	
pq	= (110) : (01̄1)	....	117 6	117 12	6
r′o′	= (2̄01) : (1̄11)	....	35 3	35 10	7
o′p	= (1̄11) : (110)	....	92 30	92 23	7
pr′	= (110) : (201̄)	....	52 24	52 27	3
r′p	= (2̄01) : (110)	....	127 36	127 33	3

Ammonium Cadmium Selenate, $(NH_4)_2Cd(SeO_4)_2 . 6H_2O$.

Crystal System.—Monoclinic.   Class No. 5, holohedral-prismatic.

Axial Angle.—$\beta = 106° 1'$.   Topsøe's value, 106° 4'.

Ratio of Axes.—$a : b : c = 0\cdot7418 : 1 : 0\cdot5026$.

Topsøe's values $0\cdot7388 : 1 : 0\cdot5001$.

Forms observed.—$a\{100\}$, $b\{010\}$, $c\{001\}$, $p\{110\}$, $p'\{120\}$, $p''\{210\}$, $p'''\{130\}$, $q\{011\}$, $r'\{\bar{2}01\}$, $o'\{\bar{1}11\}$, $n'\{\bar{1}\bar{2}1\}$.   The forms a, p'' and n', were not observed by Topsøe.

Habit.—A great variety of habits were exhibited, chiefly, however, more or less tabular parallel either $c\{001\}$ or $r'\{\bar{2}01\}$, and frequently elongated at the same time parallel to the symmetry axis b.   A common type is shown in fig. 3, $c\{001\}$ being here the plane of the Table.
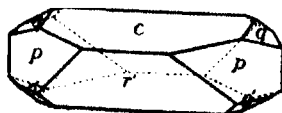
FIG. 3.—A typical crystal of ammonium cadmium selenate.

The crystals were mostly white and opaque, " porcelain-like " as Topsøe describes them.   No crystal was found entirely free from white opacity, but a considerable number of crystals were present in certain crops in which there were transparent portions, and advantage was taken of these both in the density determinations and in the optical investigation.

The table of interfacial angles is remarkably satisfactory, considering the difficulty introduced by partial opacity.   The signal-images were, indeed, very brilliant, but the limits of the values for the same angle are somewhat wider than has generally been the case in these investigations of this mono-clinic series.   The mean values, however, are absolutely trustworthy, and agree fairly well with those of Topsøe, which are given in the last column.

Interfacial Angles of Ammonium Cadmium Selenate.

Angle.	No. of measurements.	Limits.	Mean observed.	Calculated.	Diff.	Topsøe's values.
ac = (100) : (001)...	1	° ′ — ° ′	74 0	73 59	1	73 56
as = (100) : (101)...	—	—	—	45 15	—	
so = (101) : (001)...	—	—	—	28 44	—	
cr' = (001) : (2̄01)...	17	63 58– 64 25	64 15	64 17	2	64 21
cs' = (001) : (1̄01)...	—	—	—	38 40	—	
$s'r'$ = (1̄01) : (2̄01)...	—	—	—	25 37	—	
$r'a$ = (2̄01) : (100)...	2	41 37– 42 1	41 49	41 44	5	
$r'c$ = (2̄01) : (001̄)...	18	115 34–116 11	115 46	115 43	3	115 39
ap = (100) : (110)...	24	35 11– 35 44	35 30	35 30	0	
ap'' = (100) : (210)...	4	19 1– 19 55	19 36	19 38	2	
$p''p$ = (210) : (110)...	1	—	15 49	15 52	3	
pp' = (110) : (120)...	18	19 3– 19 47	19 26	19 28	2	19 28
$p'b$ = (120) : (010)...	14	34 45– 35 25	35 1	35 2	1	35 10
pp''' = (110) : (130)...	5	29 12– 29 48	29 29	29 27	2	
$p'''b$ = (130) : (010)...	8	24 45– 25 21	24 58	25 3	5	25 9
$p'p'''$ = (120) : (130)...	7	9 35– 10 19	10 2	9 59	3	10 1
pb = (110) : (010)...	23	54 15– 54 54	54 31	54 30	1	54 38
pp = (110) : (1̄10)...	17	70 43– 71 28	71 0	*	—	70 44
pp = (110) : (1̄1̄0)...	16	108 32–109 18	109 0	109 0	0	109 16
cq = (001) : (011)...	38	25 23– 26 11	25 47	*	—	25 40
qb = (011) : (010) ..	20	63 58– 64 49	64 15	64 18	2	64 20
qq = (011) : (01̄1)...	16	128 14–128 37	128 25	128 26	1	
ao = (100) : (111)...	—	—	—	48 28	—	
oq = (111) : (011)...	—	—	—	27 9	—	
aq = (100) : (011)...	—	—	—	75 37	—	
qo' = (011) : (1̄11)...	—	—	—	34 50	—	
$o'a$ = (1̄11) : (1̄00)...	—	—	...	69 33	—	
co = (001) : (111)...	—	—	—	34 20	—	
op = (111) : (110)...	—	—	—	42 41	—	
cp = (001) : (110)...	30	76 36– 77 15	77 1	*	—	76 57
po' = (110) : (11̄1)...	8	57 53– 58 28	58 9	58 5	4	
$o'c$ = (11̄1) : (001̄)...	10	44 31– 45 11	44 48	44 54	6	44 47
pc = (110) : (001̄)...	30	102 47–103 17	102 59	102 59	0	103 3
bn = (010) : (121)...	—	—	—	54 30	—	
no = (121) : (111)...	—	—	—	15 52	—	
bo = (010) : (111)...	—	—	—	70 22	—	
os = (111) : (101)...	—	—	—	19 38	—	
bn' = (010) : (1̄21)...	—	—	—	47 9	—	
$n'o'$ = (1̄21) : (1̄11)...	—	—	—	17 58	—	
bo' = (010) : (1̄11)...	8	64 50– 65 23	65 10	65 7	3	
$o's'$ = (1̄11) : (1̄01)...	—	—	—	24 53	—	24 55
$o'o'$ = (1̄11) : (1̄1̄1)...	2	49 42– 49 42	49 42	49 46	4	49 51
sq = (101) : (011)...	—	—	—	37 52	—	
qn' = (011) : (1̄21)...	1	—	35 42	35 47	5	
$n'p$ = (1̄21) : (1̄10)...	1	—	51 15	51 20	5	
qp = (011) : (1̄10)...	25	86 50– 87 29	87 9	87 7	2	87 16
ps = (1̄10) : (1̄01)...	—	—	—	55 1	—	
pq = (1̄10) : (01̄1)...	24	92 31– 93 12	92 50	92 53	3	
$s'q$ = (1̄01) : (011)...	—	—	—	45 20	—	
qn = (011) : (121)...	—	—	—	26 28	—	
np = (121) : (110)...	—	—	—	36 29	—	
qp = (011) : (110)...	31	62 36– 63 20	62 56	62 57	1	62 59
pe' = (110) : (1̄01)...	—	—	—	71 43	—	
pq = (110) : (01̄1)...	30	116 37–117 29	117 4	117 3	1	
$r'o'$ = (2̄01) : (1̄11)...	10	34 40– 35 36	35 3	35 7	4	
$o'p$ = (1̄11) : (110)...	9	92 4– 92 40	92 18	92 18	0	92 19
pr' = (110) : (2̄01)...	26	52 28– 52 57	52 41	52 35	6	52 31
$r'p$ = (2̄01) : (110)...	25	127 0–127 44	127 18	127 25	7	127 29
Total (10 crystals) ...	519					

As the only comparisons possible between the three cadmium salts are with respect to the crystal angles and elements, these can be instituted at once, and are made in the accompanying Table.

Comparison of the Interfacial Angles.

Angle.			RbCd selenate.		CsCd selenate.		AmCd selenate.	
ac	=	(100) : (001)	74	53	73	38	73	59
as	=	(100) : (101)	45	44	45	2	45	15
sc	=	(101) : (001)	29	9	28	36	28	44
cr'	=	(001) : (201)	63	49	64	31	64	17
cs'	=	(001) : (101)	38	35	38	44	38	40
s'r'	=	(101) : (201)	25	14	25	47	25	37
r'a	=	(201) : (100)	41	18	41	51	41	44
ap	=	(100) : (110)	35	33	35	6	35	30
pp'	=	(110) : (120)	19	28	19	28	19	28
p'b	=	(120) : (010)	34	59	35	26	35	2
pp'''	=	(110) : (130)	29	26	29	32	29	27
p'''b	=	(130) : (010)	25	1	25	22	25	3
p'p'''	=	(120) : (130)	9	58	10	4	9	59
pb	=	(110) : (010)	54	27	54	54	54	30
vq	=	(001) : (011)	25	53	25	41	25	47
qb	=	(011) : (010)	64	7	64	19	64	13
ao	=	(100) : (111)	48	57	48	14	48	28
oq	=	(111) : (011)	27	29	27	3	27	9
aq	=	(100) : (011)	76	26	75	17	75	37
qo'	=	(011) : (111)	34	45	35	16	34	50
o'a	=	(111) : (100)	68	49	69	27	69	33
co	=	(001) : (111)	34	45	34	9	34	20
op	=	(111) : (110)	43	0	42	31	42	41
cp	=	(001) : (110)	77	45	76	40	77	1
po'	=	(110) : (111)	57	29	58	5	58	5
o'c	=	(111) : (001)	44	46	45	15	44	54
bn	=	(010) : (121)	54	15	54	40	54	30
no	=	(121) : (111)	15	57	15	49	15	52
bo	=	(010) : (111)	70	12	70	29	70	22
os	=	(111) : (101)	19	48	19	31	19	38
bo'	=	(010) : (111)	65	15	65	12	65	7
o's'	=	(111) : (101)	24	45	24	48	24	53
sq	=	(101) : (011)	38	13	37	42	37	52
qp	=	(011) : (110)	86	23	87	37	87	7
ps	=	(110) : (101)	55	24	54	41	55	1
s'q	=	(101) : (011)	45	19	45	20	45	20
qn	=	(011) : (121)	26	48	26	20	26	28
np	=	(121) : (110)	36	48	36	28	36	29
qp	=	(011) : (110)	63	36	62	48	62	57
ps'	=	(110) : (101)	71	5	71	52	71	43
r'o'	=	(201) : (111)	34	46	35	10	35	7
o'p	=	(111) : (110)	92	55	92	23	92	18
pr'	=	(110) : (201)	52	19	52	27	52	35

Comparison of the Axial Angles and Axial Ratios.

	Axial angle.	Axial ratios.
	β.	$a : b : c$
Rubidium cadmium selenate....................	105° 7′	0·7402 : 1 : 0·5026
Ammonium ,, ,, ...	106° 1′	0·7418 : 1 : 0·5026
Cæsium ,, ,, ...	106° 22′	0·7319 : 1 : 0·5011

The angles of the rubidium and cæsium salts are related just as in the other groups of the series, the signs and amounts of the differences being similar. The angles of the ammonium salt are adequately close to those of the two metallic salts to correspond to true isomorphism, but the relation is, as usual for the ammonium salts, not a eutropic one.

Relative Density.—Four determinations were made by the immersion method, using methylene iodide and benzene mixture.

I.	Density for 16°·2/4°	......	2·4521	For 20°/4°	......	2·4512
II.	,,	16°·0/4°	......	2·4514	,,	......	2·4504
III.	,,	15°·1/4°	......	2·4498	,,	......	2·4481
IV.	,,	15°·0/4°	......	2·4521	,,	......	2·4509

Mean ...... 2·4501

Accepted value for 20°/4°......**2·450**.

Molecular Volume.—$\dfrac{M}{d} = \dfrac{538\cdot98}{2\cdot450} = 219\cdot99.$

Topsøe found the specific gravity 2·307, a value much too low, and the molecular volume correspondingly much too high, 235·3.

Molecular Distance Ratios (topic axial ratios).—

$$\chi : \psi : \omega = 6\cdot3045 : 8\cdot4988 : 4\cdot2715.$$

As much reliance as usual, however, cannot be placed on these values for the density and constants dependent on it, as no crystals absolutely transparent throughout could be obtained, the best that could be done being to use such as had the greater part of their substance transparent.

Optical Investigation.—The ordinary procedure could not be followed with the optics for the same reason, that the best crystals were only transparent in parts, the remaining portions being white and opaque like porcelain. The grinding of surfaces for the preparation of plates and prisms was a very difficult task, as opaque portions gave way, and, even when a surface was successfully ground through a transparent part, it rapidly became opaque. After many fruitless efforts, one good 60°-prism, correctly orientated to afford the α and γ indices directly, was, however, successfully ground, and, when fitted with miniature balsam-cemented glass plates, proved beautifully transparent through a sufficient portion of its extent, and gave two excellent spectra corresponding to α and γ. Another prism, a natural one formed by

two faces of $q\{011\}$, was also provided by a crystal, one end of which, where *these faces were situated, was quite transparent;* when this prism was also fitted with glass plates, it afforded two excellent spectra, one spectrum affording β directly, and the other a value near, but not exactly, γ.

The determination of the two refractive indices of this prism thus afforded accurate information as to the intermediate refractive index β of the crystal, and was carried out first, so as to enable a liquid to be chosen which had practically the same index as the mean index for the crystal, monochlorobenzene being indicated. One excellent crystal tabular parallel to $c\{001\}$, like fig. 3, which had been obtained during a very cold night, and which was transparent through a sufficient extent and remained so adequately long, was then used, immersed in this liquid, for (1) the determination of the positions of the two median lines, the bisectrices of the optic axial angle and the axes of the optical ellipsoid lying in the symmetry plane, by observations of the optic axial interference figure; (2) the measurement of the true angle between the optic axes within the crystal; and (3) the determination of the dispersion of the median lines. The knowledge thus obtained of the positions of the axes of the ellipsoid (the third axis of the optical ellipsoid being fixed by the monoclinic symmetry, being the symmetry axis b itself) enabled the refractive index near γ, afforded as the second index by the natural prism formed by two $q\{011\}$ faces, to be corrected to the true value of γ. The value of γ thus obtained proved to be practically identical with that derived directly from the ground prism affording α and γ. In this manner the whole of the optical constants were eventually obtained, and the results are summarised as follows :—

Orientation of Optical Ellipsoid.—The plane of the optic axes is $b\{010\}$, and the sign of the double refraction is positive. The axis α of the indicatrix
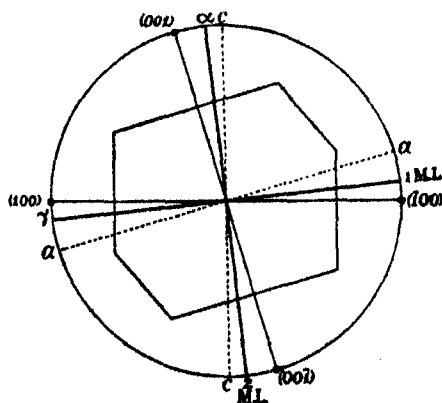
Fig. 4

(ellipsoid) is the second median line, and lies 10° 1' behind the normal to
$c\{001\}$, near to the vertical axis c. As the normal to $c\{001\}$ is 16° 1' in front
of the vertical axis the second median line is 6° 0' in front of the c-axis.
The first median line γ is 10° 1' above the inclined axis a. Both median
lines thus lie in the obtuse angle ac. Fig. 4 will render the situation clear.

Optic Axial Angle.—The values for the true optic axial angle, as measured
while the crystal was immersed in monochlorobenzene, were as under, the
obtuse angle $2V_o$ being that actually measured, and the values for the acute
angle $2V_a$ being given alongside.

Light.	2V$_o$.	2V$_a$.
Li	103 55	78 5
C	103 49	76 11
Na	103 29	76 31
Tl	103 11	76 49
Cd	103 0	77 0
F	102 47	77 13

Dispersion of the Median Lines.—The median lines showed an extremely
small amount of dispersion in the symmetry plane, about 3 minutes being
indicated, which is the limit of experimental error.

Refractive Indices.—

Refractive Indices of Ammonium Cadmium Selenate.

Light.	α.	β.	γ.
Li	1·5167	1·5221	1·5311
C	1·5172	1·5227	1·5317
Na	1·5206	1·5260	1·5352
Tl	1·5242	1·5296	1·5386
Cd	1·5262	1·5315	1·5408
F	1·5283	1·5338	1·5427
G	1·5340	1·5393	1·5485

Mean of a, β, and γ for Na light = 1·5273.

a = Vibration direction parallel to second median line, 6° 0' in front of vertical axis c.
β =   „   „   „   symmetry axis b.
γ =   „   „   „   first median line, 10° 1' above inclined axis a.
Double refraction, $Na_{\gamma-a}$ = 0·0146.

General formula for β, corrected to a vacuum :—

$$\beta = 1\cdot5090 + \frac{619\ 700}{\lambda^2} - \frac{543\ 700\ 000\ 000}{\lambda^4} + \dots$$

The a indices are equally well reproduced by the formula if the constant
1·5090 be diminished by 0·0054, and the γ indices if it be increased by
0·0091.

Axial Ratios of the Optical Ellipsoid.—

$$\alpha : \beta : \gamma = 0.9965 : 1 : 1.0061, \qquad \mathfrak{a} : \mathfrak{b} : \mathfrak{c} = 1.0035 : 1 : 0.9940.$$

Molecular Optical Constants.

	Axis of optical indicatrix.		α.	β.	γ.
Lorenz	Specific refraction, $\dfrac{n^2-1}{(n^2+2)d} = \mathfrak{n}$	C	0·1235	0·1246	0·1264
		G	0·1269	0·1279	0·1297
	Molecular refraction, $\dfrac{n^2-1}{n^2+2} \cdot \dfrac{M}{d} = \mathfrak{m}$.	C	66·57	67·17	68·14
		G	68·38	68·95	69·92
	Specific dispersion, $\mathfrak{n}_G - \mathfrak{n}_C$		0·0034	0·0033	0·0033
	Molecular dispersion, $\mathfrak{m}_G - \mathfrak{m}_C$		1·81	1·78	1·78
Gladstone ...	Molecular refraction, $\dfrac{n-1}{d} M$ C		113·78	114·99	116·97

Mean molecular refraction (Gladstone), $\frac{1}{3} (\alpha + \beta + \gamma) = 115.25$.

General Conclusions concerning the Cadmium Group.

So far as the crystals of this group of three salts have lent themselves to investigation the results are in line with those derived from all the other groups of monoclinic hexahydrated double sulphates and selenates. As regards the crystal angles and elements, which are the only constants that have been completely determinable for all three salts, the relationships are precisely those afforded by the other groups. Hence, if the potassium salt were obtainable the three alkali metallic salts would undoubtedly form a eutropically isomorphous series. The ammonium salt is isomorphous but not eutropic with the alkali metallic salts of the group.

General Remarks on Completion of the Research.

The two papers now published on the manganese and cadmium groups of double selenates form the completion of the task which the author set himself in the year 1890, namely, the thorough detailed investigation of the crystals of the rhombic sulphates and selenates of the alkalies, $R_2{}^{S}_{Se}O_4$, in which R is potassium, rubidium, cæsium, ammonium and thallium, and of the monoclinic hexahydrated double sulphates and double selenates, $R_2M({}^{S}_{Se}O_4)_2.6H_2O$, in which R represents the same alkali bases and M is magnesium, zinc, iron, nickel, cobalt, copper, manganese and cadmium. Only two of the double salts containing thallium, those in which zinc is the M-metal, have proved suitable as regards perfection of the crystals for inclusion in this research. But, including a group of three analogous double chromates, seventy-five salts in all have been investigated. The work has involved the complete measurement of over 800 crystals (involving altogether 45,000 goniometrical measurements), selected for their special perfection from many crops of each

salt, grown under ideal conditions. Over 500 determinations of crystal density have been carried out. More than 2,000 truly plane and accurately orientated polished surfaces have been produced—with the aid of the most efficient and indispensable cutting and grinding goniometer designed for the purpose and described to the Royal Society in the year 1895—in the course of the preparation of the section-plates and 60°-prisms required for the optical portion of the investigation. Moreover, all the optical constants have been determined for a considerable number of specific wave-lengths of light, with the aid of the spectroscopic monochromatic illuminator also devised for the work and described to the Royal Society in 1895, the electric arc being the source of light. The whole has been carried out by the author personally with the exception of the portion concerning the three double chromates, which was carried out jointly by the author and Miss Mary W. Porter. It will now be obvious why the research has occupied so many years, and it is a matter of the deepest satisfaction to the author that he has been permitted to complete it. The results have been published in twenty-six memoirs, besides six other papers describing the new instruments designed specially for this work, but all of which have proved of general application not only to crystallographic but also to ordinary physical investigation and measurement. A complete and chronological list of these memoirs, with full references, is given in an appendix to this paper (p. 262).

The most satisfactory feature of the results is the absolutely unanimous manner in which the individual results for the nineteen different groups confirm each other as regards the relationships of the potassium, rubidium and cæsium salts and the positions of the ammonium and thallium salts of the group. The main conclusions derived from the whole investigation are thus confirmed nineteen times over.

The first of these main conclusions is that the interfacial angles of the crystals, their elements and habits, the volumes and edge dimensions of their space-lattice unit cells, the dimensions and orientations (where variable, in the monoclinic salts) of their optical ellipsoids, their refractive power, the amount of their double refraction, their molecular refractions, their thermal dilatations in the cases where they were determinable (the rhombic simple sulphates), and indeed the minutest details of the structural and physical properties of the crystals, all exhibit a regular progression with the atomic number of the alkali metal ($K = 19$, $Rb = 37$, $Cs = 55$, a difference of eighteen at each step). Indeed, this invariable rule may be considered as a definite law of progression for these rhombic anhydrous oxy-salts of the alkalies and the monoclinic hexahydrated double oxy-salts containing these same alkali bases as the dominating constituents.

The difference in atomic number, eighteen, between potassium and rubidium, and between the latter and cæsium, is interesting; for it corresponds exactly to a whole shell of electrons, according to the Lewis-Langmuir version of the atomic structure theory (or to two shells according to the Bohr-Sommerfeld version). That is to say, when we pass from potassium to rubidium, and again from rubidium to cæsium, we are adding another complete shell of electrons to the structure of the atom, and are obviously adding thereby to the diameter of the atom. Now W. L. Bragg has shown that the atomic diameter is a periodic function of the atomic number, and that the curve representing the atomic diameters of the elements has very sharp maxima at the positions occupied on the curve by the electropositive alkali metals, and more extended minima at the positions of the electronegative elements and of those dyad-acting metals which form weakly acidic or only feebly basic oxides (the M-metals of the monoclinic double salts). The curve of atomic diameters is reproduced in fig. 5 in order to make this point quite clear.
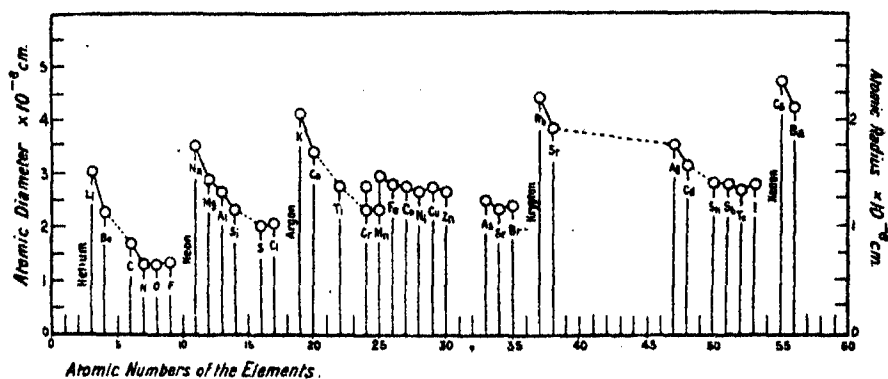
Fig. 5.—The curve of atomic diameters.

Hence these two facts combine to cause the two series of salts chosen for this investigation to be the very best that could possibly have been so selected for the purpose of exhibiting to its greatest extent, and, therefore, most clearly, any differences of crystal form and properties which may be brought about by replacing one element by another of the same family group so as to form another member of the isomorphous series. The fact that the atom of the alkali metal alters in size by a whole electronic shell at each successive interchange, passing thereby from one maximum of the curve to another, higher each time on account of the additional diameter conferred, is thus seen to be the direct cause of the alteration (expansion) of the crystal structure; that is, it is the cause of the alteration of the dimensions of the space-lattice cells, and correspondingly of the perceptible change in the crystal angles (the

symmetry remaining the same) and in the optical and other physical properties. Moreover, just as the law of atomic diameters of W. L. Bragg explains completely the author's main result so astonishingly simply, so conversely does this result confirm the accuracy of the law of atomic diameters. Fundamentally, we must go back still further, however, to the law of Moseley, to the fact that the increase of one unit in atomic number means unit accretion of mass (approximately two of atomic weight) and of positive electric charge on the nucleus of the atom and the corresponding addition of a negative electron to the exterior, as the ultimate cause of the progression in the crystallographic properties. Whether we adopt the conception of the sharing of electrons (in the cases of electronegative elements) of the Langmuir version of the atomic structure theory, or the modification thereof by Sir J. J. Thomson, which requires no sharing of electrons, there can be no doubt that no sharing of electrons occurs in the case of the alkali metals. Potassium, rubidium and cæsium possess respectively (as their atomic numbers 19, 37 and 55 indicate) one more electron than required to produce the stable shells of argon (atomic number 18), krypton (atomic number 36), and xenon (atomic number 54). This one extra electron obviously occupies space outside the complete inert gas shell, and is doubtless the monadic valency link or active chemically combining agency characteristic of an alkali metal in the chemical combination with an electronegative element probably actually passing over to the latter, which lacks one or more electrons to complete a stable shell. All versions of the atomic structure theory agree on this. Hence it is that the alkali metals occupy the maxima of the atomic diameter curve, cæsium indeed having the greatest of all the atomic diameters measured, and the change of diametral dimension on passing from one to another is also commensurably considerable, corresponding as already stated to the addition of a shell of eighteen electrons.

Thus it comes about that the choice made in the year 1890, of suitable isomorphous series for studying the changes of crystal structure and properties brought about by the interchange of the replaceable elements of the same family group, has proved so fortunate. At that time we had no inkling of the wonderful nature of the chemical atom, and the manner in which the results of the investigation agree with what could be expected, from atoms constructed as we now know them to be, is highly satisfactory. Moreover, the remarkably dominant influence of the alkali metal in the double salts, compared with the dyad-acting metal, is rendered readily comprehensible.

The second main conclusion is that in every one of the nineteen groups the crystals of the ammonium salt have proved to be practically isostructural with those of the rubidium salt of the same group. This fact has recently

been used by A. O. Rankine* to furnish proof of the Langmuir version of the atomic structure theory.   For (if that version be correct) as krypton should bear the same relation to rubidium as methane CH_4 does to ammonium NH_4, an atom of krypton should have the same volume as a molecule of methane. Rankine has actually determined the volumes by the viscosity method, and found this to be the case.

A third main conclusion is that the thallium salt of any group also crystallographically resembles the ammonium salt, in being isomorphous but not eutropic (following the law of progression) with the alkali salts, and also in being nearly isostructural with the rubidium salt.   The crystals of the thallium salts, however, are sharply distinguished by possessing transcendent refractive power.

The results of this investigation may also be said to have finally settled the old Haüy-Mitscherlich controversy.   For they prove that each of even the most similar substances—the members of isomorphous series—is endowed with its own distinctive crystal form and properties.   As regards even cubic crystals, for which the angles are fixed by the high symmetry, this is true as regards the physical properties.   The work of Sir Henry A. Miers† on the rhombohedral red silver ores, proustite, Ag_3AsS_3, and pyrargyrite, Ag_3SbS_3, proved this for crystal angles, the rhombohedral angles for the two iso-morphous substances being respectively 72° 12′ and 71° 22′.   But the author's results go further in showing that not only are there real differences of crystal angle between even the most similar non-cubic substances, but that in the case of the most important series of isomorphous oxy-salts formed by the alkali metals the differences exhibit a definite progression with the atomic number of the alkali metal, and thus obey a definite law.   The maximum difference of angle observed by the author has been 2° 28′, which occurred between potassium copper and cæsium copper selenates.   Moreover, the term "isomorphism" must not be taken absolutely literally, but to mean similarity of a kind which permits these definite small differences of crystal angle, while the symmetry remains identical.

One further result of this investigation has been to show conclusively that —in the cases of members of isomorphous series, for which the type of structure must be identical throughout the series the symmetry being the same—real value attaches to the physical constant molecular volume, the quotient of the molecular weight by the density of the crystals, and to the conception of topic axial ratios or distance ratios, derived by combining the molecular volume with the axial ratios of the crystals.   This necessarily

* 'Nature,' vol. 108, p. 219 (1921).

† 'Min. Mag.,' vol. 8, p. 37 (1888).

implies the great importance of including density determinations of great accuracy in all such crystallographic investigations. For the molecular volume is a relative measure of the volume of the unit cell of the space-lattice of the crystal structure, and the topic axial ratios are the relative measures of the linear edge-dimensions of this unit cell, or the distances (hence the term distance ratios) between the node points of the lattice along the three axial directions. These measures are correctly relative not only for the three sets of edges of the cell of the same substance, but also for the edges of the cells throughout the whole series. This unit cell of the space-lattice is the habitat of the grosser structural unit of the crystal, which is usually the chemical molecule or a small number, two, three or four being common numbers, of chemical molecules; the regular repetition of the representative points, or centres of gravity, of such grosser units forms the space-lattice.

The final proof that this is absolute fact was afforded by the X-ray analysis of the rhombic sulphates of potassium, rubidium, cæsium and ammonium, which was carried out with the author's crystals in the laboratory of Sir William Bragg, by Prof. A. Ogg and Mr. F. L. Hopwood.* For the absolute measurements of the spacings and cell dimensions, which they obtained with the X-ray spectrometer, exhibited precisely the relative values published previously by the author. Incidentally also, this X-ray work proved that the second main conclusion of the author above elaborated, that the ammonium salts are almost perfectly isostructural with the analogous rubidium salts is also an absolute fact, and that there could be no possibility of the ammonium salt being built on a different scale, with merely similar relative values. For the absolute values found by X-ray spectrometric analysis, both for the cell volume and cell-edge dimensions, of rubidium and ammonium sulphates, were almost exactly the same. The author used this result, in a special memoir,† finally to disprove the valency volume theory of Pope and Barlow, which required that the volume of ammonium sulphate should be twenty-four, twice that of the rubidium salt, which would be twelve. This conclusion has since been confirmed by W. L. Bragg, who has fixed the sizes of the atoms of a considerable number of the chemical elements, and represented them in his curve of atomic diameters, already referred to and illustrated in fig. 5. These atomic dimensions are totally different from those stipulated by the valency volume theory. A striking example is that offered by a comparison of the sizes of the atoms of cæsium and of nitrogen. According to the valency volume theory cæsium should only have a volume of one, corresponding to its monadic valency, whereas nitrogen should have a

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* 'Phil. Mag.,' vol. 32, p. 518 (1916).
† 'Roy. Soc. Proc.,' A, vol. 93, p. 72 (1917).

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volume of three times as much, corresponding to its triadic valency. The truth is, however, just the other way round, for cæsium possesses the largest diameter of any element measured (see the last maximum on the curve, fig. 5), namely, 4.75×10^{-8} cm. while nitrogen has only an atomic diameter of 1.30×10^{-8} cm., less than a third of the diameter of the atom of cæsium. The law of atomic diameters now, therefore, replaces the valency volume theory; for the idea that the size of the atoms has much to do with crystal structure was sound, but the real sizes are far removed from what was supposed by the valency volume theory, namely, that they were proportional to the valency of the element. With this law of atomic diameters of W. L. Bragg, however, the author's results have been shown to be in full agreement.

Thus it has come about, by the time that the author has completed his crystallographic investigation of these important isomorphous series, that a full explanation of the results is afforded by the immense amount of real knowledge that has been accumulated during the same time concerning the structure and nature of the chemical atom, and that revealed by means of the powerful new weapon of research, analysis by means of X-rays, from which the law of atomic diameters has been derived. It is thus highly satisfactory that the work of Moseley, Sir J. J. Thomson, Langmuir, the Braggs and the author should so perfectly agree in giving us a wider and fuller understanding of the nature of crystals, and of the structure of the solid matter of which they are the organised expression, than could have been expected or anticipated at the time when the author's researches on these isomorphous series were initiated.

APPENDIX.

List of Memoirs Communicating the Results of the Research.

1. Connection between the atomic weight of contained metals and the magnitude of the angles of crystals of isomorphous salts. A study of the potassium, rubidium, and cæsium salts of the monoclinic series of double sulphates $R_2M (SO_4)_2.6H_2O$.

'Journ. Chem. Soc. Trans.,' vol. 63, p. 337 (1893); 'Z. f. Kryst.,' vol. 21, p. 491 (1893).

2. Connection between the atomic weight of contained metals, and the crystallographical characters of isomorphous salts. A comparative crystallographical study of the normal sulphates of potassium, rubidium and cæsium.

'Journ. Chem. Soc. Trans.,' vol. 65, p. 628 (1894); 'Z. f. Kryst.,' vol. 24, p. 1 (1895).

3. The volume and optical relationships of the potassium, rubidium and cæsium salts of the monoclinic series of double sulphates.

'Journ. Chem. Soc. Trans.,' vol. 69, p. 344 (1896); 'Z. f. Kryst.,' vol. 27, p. 113 (1897).

4. Comparison of the results of the investigations of the simple and double sulphates containing potassium, rubidium and cæsium, and general deductions therefrom concerning the influence of atomic weight on crystal characters.

'Journ. Chem. Soc. Trans.,' vol. 69, p. 495 (1896); 'Z. f. Kryst.,' vol. 27, p. 252 (1897).

5. The bearing of the results of the investigations of the simple and double sulphates containing potassium, rubidium and cæsium on the nature of the structural unit.

'Journ. Chem. Soc. Trans.,' vol. 69, p. 507 (1896) ; ' Z. f. Kryst.,' vol. 27, p. 266 (1897).

6. A comparative crystallographical study of the normal selenates of potassium, rubidium and cæsium.

'Journ. Chem. Soc. Trans.,' vol. 71, p. 846 (1897) ; 'Z. f. Kryst.,' vol. 29, p. 63 (1898).

7. The thermal deformation of the crystallised normal sulphates of potassium, rubidium and cæsium.

'Phil. Trans.,' A, vol. 192, p. 455 (1899) ; ' Z. f. Kryst.,' vol. 31, p. 426 (1899).

8. A comparative crystallographical study of the double selenates of the series $R_2M(SeO_4)_2.6H_2O$. Salts in which M is zinc.

'Proc. Roy. Soc.,' A, vol. 66, p. 248, and vol. 67, p. 58 (1900) ; ' Z. f. Kryst.,' vol. 33, p. 1 (1900).

9. A comparative crystallographical study of the double selenates of the series $R_2M(SeO_4)_2.6H_2O$. Salts in which M is magnesium.

'Phil. Trans.,' A, vol. 197, p. 255 (1901) ; ' Z. f. Kryst.,' vol. 35, p. 529 (1902).

10. Crystallised ammonium sulphate and the position of ammonium in the alkali series.

'Journ. Chem. Soc. Trans.,' vol. 83, p. 1049 (1903) ; ' Z. f. Kryst.,' vol. 38, p. 602 (1904).

11. The relation of ammonium to the alkali metals. A study of ammonium magnesium and ammonium zinc sulphates and selenates.

'Journ. Chem. Soc. Trans.,' vol. 87, p. 1123 (1905) ; ' Z. f. Kryst.,' vol. 41, p. 321 (1905).

12. Topic axes, and the topic parameters of the alkali sulphates and selenates.

Journ. Chem. Soc. Trans.,' vol. 87, p. 1183 (1905) ; ' Z. f. Kryst.,' vol. 41, p. 381 (1905).

13. Ammonium selenate and the question of isodimorphism in the alkali series.

'Journ. Chem. Soc. Trans.,' vol. 89, p. 1059 (1906) ; ' Z. f. Kryst.,' vol. 42, p. 529 (1907).

14. The relation of thallium to the alkali metals. A study of thallium sulphate and selenate.

'Proc. Roy. Soc.,' A, vol. 79, p. 351 (1907) ; ' Z. f. Kryst.,' vol. 44, p. 113 (1907).

15. The relation of thallium to the alkali metals. A study of thallium zinc sulphate and selenate.

'Proc. Roy. Soc.,' A, vol. 83, p. 211 (1909) ; ' Z. f. Kryst.,' vol 48, p. 190 (1910).

16. Crystallographic constants and isomorphous relations of the double chromates of the alkalies and magnesium (in collaboration with Miss Mary W. Porter).

'Mineralog. Mag.,' vol. 16, p. 169 (1912) ; ' Z. f. Kryst.,' vol. 51, p. 53 (1912).

17. Ammonium ferrous sulphate and its alkali-metal isomorphs.

'Proc. Roy. Soc.,' A, vol. 88, p. 361 (1913) ; ' Z. f. Kryst., vol. 52, p. 433 (1913).

18. The monoclinic double sulphates containing ammonium. Completion of the double sulphate series.   'Phil. Trans.,' A, vol. 216, p. 1 (1915).

19. Monoclinic double selenates of the nickel group.

'Phil. Trans.,' A, vol. 217, p. 199 (1917).

20. X-ray analysis and topic axes of the alkali sulphates, and their bearing on the theory of valency volumes.   'Proc. Roy. Soc.,' A, vol. 93, p. 72 (1917).

21. Selenic acid and iron. Reduction of selenic acid by nascent hydrogen and hydrogen sulphide. Preparation of ferrous selenate and double selenates of iron group.

'Proc. Roy. Soc.,' A, vol. 94, p. 352 (1918).

22. Monoclinic double selenates of the iron group.

'Phil. Trans.,' A, vol. 218, p. 395 (1919).

23. Monoclinic double selenates of the cobalt group.

'Proc. Roy. Soc.,' A, vol. 96, p. 156 (1919).

24. Monoclinic double selenates of the copper group.

'Proc. Roy. Soc.,' A, vol. 98, p. 67 (1920).

25. Monoclinic double selenates of the manganese group.
          'Proc. Roy. Soc.,' A, vol. 101, p. 225 (1922).
26. Monoclinic double selenates of the cadmium group.
          'Proc. Roy. Soc.,' A, vol. 101, p. 245 (1922).

MEMOIRS CONCERNING NEW INSTRUMENTS FOR THE RESEARCH.

1. An instrument for grinding section-plates and prisms of crystals of artificial preparations accurately in the desired directions.
          'Phil. Trans.,' A, vol. 185, p. 887 (1895) ; ' Z. f. Kryst.,' vol. 24, p. 433 (1895).
2. An instrument of precision for producing monochromatic light of any desired wavelength, and its use in the investigation of the optical properties of crystals.
          'Phil. Trans.,' A, vol. 185, p. 913 (1895) ; ' Z. f. Kryst.,' vol. 24, p. 455 (1895).
3. An instrument for cutting, grinding and polishing section plates and prisms of mineral or other crystals accurately in the desired directions.
          'Proc. Roy. Soc.,' A, vol. 57, p. 324 (1895) ; ' Z. f. Kryst.,' vol. 25, p. 79 (1896).
4. A compensated interference dilatometer.
          'Phil. Trans.,' A, vol. 191, p. 313 (1898) ; ' Z. f. Kryst.,' vol. 30, p. 529 (1899).
5. Verbesserungen an den Apparate zum Schneiden, Schleifen, und Poliren genau orientirter Krystallplatten.   ' Zeitschr. für Kryst.,' vol. 31, p. 458 (1899).
6. The elasmometer, a new interferential form of elasticity apparatus.
          'Phil. Trans.,' A, vol. 202, p. 143 (1904) ; ' Z. f. Kryst.,' vol. 39, p. 321 (1904).

Magnetism and Atomic Structure.—II.   *The Constitution of the Hydrogen-Palladium System and other similar Systems.*

By A. E. OXLEY, M.A., D.Sc., F.Inst.P.

(Communicated by A. W. Porter, F.R.S.   Received August 17, 1921.)

1. INTRODUCTION.

The present work is a continuation of that published in 'Phil. Trans., A, vol. 214, pp. 109–146 (1914); A, vol. 215, pp. 79–103 (1915); A, vol. 220, pp. 247–289 (1920); ' Roy. Soc. Proc.,' A, vol. 95, p. 58 (1918), and A, vol. 98, p. 264 (1921). It was believed that a magnetic examination of the properties of palladium black which had been charged with hydrogen would enable us to decide which of the proposed constitutions is the correct one. If the hydrogen were in the atomic state and *free*, one might expect that the system would be more magnetic than uncharged palladium black, whether the assumed constitution of the hydrogen atom be that of Bohr[*] or

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[*] Sommerfeld, ' Atombau u. Spectrallinien,' p. 239, *et seq.*

that proposed by the author.* If the contained hydrogen were in the molecular form, either in the state of a gas or condensed to a liquid, since gaseous and liquid hydrogen are both diamagnetic,† we should expect a diminution of the magnetic property of the system by a small amount, depending on the minute diamagnetic susceptibility of molecular hydrogen and the amount of gas occluded. Lastly, if the hydrogen enters into combination with the palladium, or is associated with the palladium so as to form a type of loose chemical compound, we should, in the light of previous knowledge of the effects of chemical combination on magnetic susceptibility, expect a change depending on the nature of the compound formed.

It is impossible here to go into details regarding the vast amount of work which has been undertaken to solve the problem of gaseous occlusion. Reference is made to the General Discussion held by the Faraday Society on the subject.‡ It will be convenient to summarise here the diverse views at present held as to the nature of the complex process of occlusion.§ These have been given by A. W. Porter‖ under the following six heads :—

(1) Chemical combination of the gas with the metal.

(2) Simple solid solution, either separately or in conjunction with (1).

(3) Two solid solutions in contiguous phases.

(4) Solution accompanied by surface adsorption.

(5) Surface condensation under molecular forces unaccompanied by solution.

(6) Simple inclusion of the gas in the interstices of the metal.

2. Experimental Determination of the Magnetic Properties of Palladium treated with Hydrogen.

The apparatus used was a modification of that described in 'Phil. Trans.,' A, vol. 214, p. 112 (1914), with the following differences. On account of the high susceptibility of pure palladium compared with that of the substances which were investigated in the earlier work, it was decided to abandon the delicate bifilar suspension mirror. Instead, a tele-microscope, focussed on

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* 'Nature,' vol. 105, p. 327 (1920). It is not inconceivable that the electron in the *free* hydrogen atom may move up into an orbit in the nuclear plane, a modification determined by conditions of symmetry.

† T. Soné, 'Science Reports, Tohoku,' vol. 8, p. 115, 1919 (for gaseous H $\chi = -19\cdot8 \times 10^{-7}$); K. Onnes, 'Proc. Amsterdam Acad.,' vol. 14, p. 121, 1911 (for liquid H $\chi = -27 \times 10^{-7}$).

‡ 'Trans. Faraday Soc.,' vol. 14, Part III (1919).

§ In what follows, "occlusion" is used in a general way to include the rapid process of adsorption and the slower process of absorption or diffusion. McBain uses the term *sorption* in the same sense.

‖ *Ibid.*, p. 192.

the support A'* carrying the specimen, was used. A nul method was adopted, the force exerted on the specimen being counterbalanced by the torsion of the phosphor-bronze strip and read off on the torsion head.

The sighting arrangement is shown in fig. 1. To prevent disturbance on the suspended system due to air currents, a brass cylinder, cut so as to fit over the pole-pieces and slotted so that it could be readily placed in position
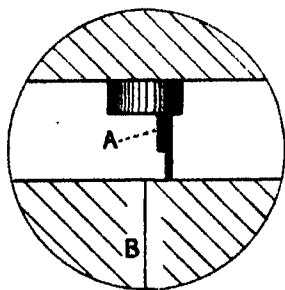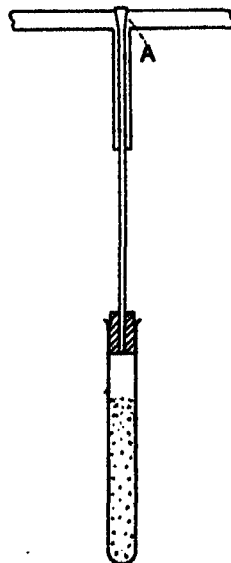
FIG. 1.   FIG. 2.

when the specimen was attached to the point A of the torsion arm, was provided. The setting of the torsion head was adjusted so that the left side of the vertical support carrying the specimen was coincident with the setting line B, as viewed through the tele-microscope.

The phial in which the specimen was placed, shown in fig. 2, consisted of a thin-walled glass tube 0·63 cm. diameter and 4·75 cm. long.

Preparation of the Hydrogen-Palladium Specimens.

The author is indebted to Dr. F. P. Burt for the loan of 2 grms. of palladium black. This was divided into two approximately equal parts, one of these being charged with hydrogen in the apparatus shown in fig. 3. The activity of the specimens was considerable, and the particles of charged palladium showed vivid flashing when they struck the walls of the tube.

The other half of the palladium was not treated. Its susceptibility was

* See fig. 2 and 'Phil. Trans.,' *loc. cit.*, fig. 2.

practically identical with that obtained by previous investigators for pure palladium, indicating that this portion was free from occluded hydrogen or
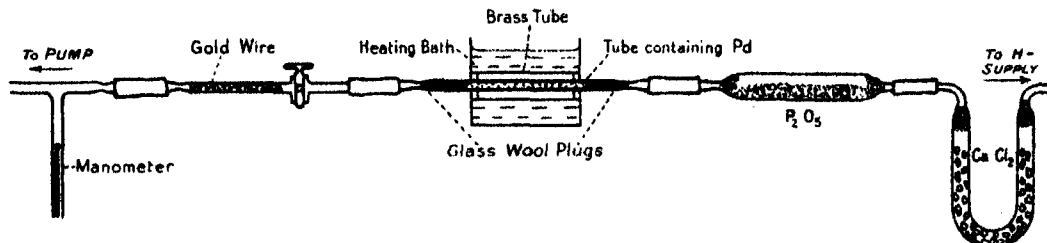
Fig. 3.

combined oxygen, at least to any measurable extent. Subsequent experiments, in which this sample was treated with hydrogen, heated to over 200° C. and the hydrogen pumped off, gave products whose susceptibility did not differ from that of the untreated one by more than 1 per cent.

Measurement of the Specific Susceptibility (χ) *of the Specimens.*

The equation for calculating this quantity is[*]

$$\chi = \frac{1}{M} \cdot \left[\chi_a \cdot M_a + (\chi_w \cdot m_w - \chi_a \cdot m_a) \cdot \frac{\vartheta - \vartheta_1}{\vartheta_2 - \vartheta_1} \right] \dots, \qquad (1)$$

where ϑ_1 is the torsion due to phial and contained air,

ϑ_2 is the torsion due to phial and contained water,

ϑ is the torsion due to phial and contained specimen,

χ_a is the specific susceptibility of air,

χ_w is the specific susceptibility of water,

χ is the specific susceptibility of specimen,

M is the mass of specimen,

• M_a is the mass of air filling the same volume as the specimen,

m_w is the mass of water,

m_a is the mass of air filling the same volume as the water.

The values of χ_w and χ_a were taken as -7.25×10^{-7} and 210×10^{-7} (at 20° C.) respectively.

In the following Tables, Z_0 is the zero of the torsion head reading, Z_1 the reading when the phial had been brought back to its initial position, ϑ, ϑ_1 and ϑ_2 the torsion necessary to balance the force on the phial when the latter was filled with the substance, air and water respectively. All the experiments (see Table I) were made at room temperature 17°–19° C., and each of the readings recorded is the mean of several determinations which agreed to within 2 per cent.

[*] *Cf.* 'Phil. Trans.,' A, vol 214, p. 114 (1914).

Table I.

Experiment.	Weight.	Z_0.	Z_1.	Z_0.	9.	9_1.	9_2.	H (gauss).	Remarks.
	grm.								
I—(a) Pd—black charged with hydrogen	0·838	260	3×360—338	260	1158	—	—	3200	Phial replaced.
(b) Pd—black, uncharged	0·838	258	3×360—323	258	1145	—	—	3200	Torsion head reset.
	0·933	253	4×360—217	252	1766	—	—	3200	Phial replaced.
	0·933	230	4×360—199	230	1769	—	—	3200	"
	0·933	230	4×360—212	230	1782	—	—	3200	"
(c) Repeated (a) after 24 hours, +14 hours	0·838	232	3×360—122	232	1830	—	—	3200	After 24 hours' exposure to air.
(d) Phial filled with air	2·052	230	3×360—204	231	1414	356	—	3200	" 38 " "
	2·052	230	1×360—225	230	—	350	—	3200	Phial replaced.
(e) Phial filled with water	3·199	228	1×360—220	230	—	—	155	3200	"
	3·199	229	23	228	—	—	144	3200	" "
			13	229	—	—	—	3200	
II—(f) Pd—black charged with hydrogen	0·909	29	328	29	299	—	—	2000	Torsion head reset.
(g) Pd—black, uncharged	0·909	29	326	29	297	—	—	2000	Phial replaced.
	0·829	28	383	28	354	—	—	2000	"
	0·829	28	374	28	346	—	—	2000	" "
	0·829	28	371	28	343	—	—	2000	" "
(h) Phial filled with air	2·056	28	114	28	—	86	—	2000	
(i) Phial filled with water	3·135	29	76	29	—	—	47	2000	

Table II.

Experiment.	Weight.	Z_0.	Z_1.	Z_0.	9.	9_1.	9_2.	H (gauss).	Remarks.
	grm.								
V.—(j) Pd—black charged with hydrogen, sealed tube	0·658	26	162	26	136	—	—	2000	Phial replaced.
	0·658	27	164	27	137	—	—	2000	" "
	0·658	28	164	28	136	—	—	2000	" "
(k) Sample (j) after the hydrogen had been pumped off	0·658	28	278	28	250	—	—	2000	" "
	0·658	28	275	28	247	—	—	2000	
	6·130	29	272	29	244	—	—	2000	
(l) Phial filled with air	6·130	29	184	29	—	105	—	2000	"
		29	134	29	—	106	—	2000	"
(m) Phial filled with water	7·270	29	106	29	—	—	76	2000	"
	7·270	29	105	29	—	—	76	2000	"

A third and fourth series of experiments similar to I and II have been made. The results agreed with those given above, and showed that the deflections obtained with the "activated" palladium were always less than those for the pure palladium.

The Hydrogen-Content of the Charged Samples.

At the conclusion of the second, third, and fourth series of tests, the palladium was transferred to a glass tube, sealed at one end, and connected through the tube containing gold wire, to a manometer and Topler pump. The palladium was heated, and the hydrogen given off collected and measured. All the palladium samples had been subjected to hydrogen at a pressure a little greater than atmospheric for an hour and three quarters, and allowed to cool in contact with the gas. From 0·83 grm. of palladium black, the volume of gas collected was 20, 17, and 15 c.c. in the three cases. The occlusion capacity is usually referred to palladium in the crystalline state, whose density is 11·4, so that, at the close of the magnetic experiments, 0·08 c.c. of palladium contained 20, 17, and 15 c.c. of hydrogen, or the palladium contained 250, 212, and 188 times its own volume of hydrogen. This is a small amount, but the loss is due in the main to the combination of the active hydrogen with the oxygen of the air, as evidenced by the dampness of the specimens and the change in appearance from a metallic lustre to coal-black. A further loss resulted from mechanical disturbance during the transference to and from the phial and charging and discharging tubes. The flashing which took place and the heat evolved were noticeable. An estimate of the hydrogen loss through the formation of water was made with the last of the above specimens. This was weighed in the damp state and in the dry state after the hydrogen had been pumped off. A difference of 0·097 grm. was found.* This corresponds to a loss of about 120 c.c. of hydrogen, so that, in the initial stage, the samples would probably contain 300–350 times their own volume of hydrogen, the loss due to mechanical disturbance being an uncertain amount.

Experiments with Sealed Tube.

An attempt was made to prevent loss of hydrogen due to chemical combination with the oxygen of the air as well as that due to mechanical disturbance of the specimen.

The phial used, shown in fig. 4, consisted of an outer glass tube, 9 mm.

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* Magnetically, this amount of water would have no effect on the measurements, the specific susceptibility of water being $-7·25 \times 10^{-7}$. Further, the mass effect does not come in because the specimens were weighed before exposure to the air took place.

diameter and 7·8 cm. long. The palladium specimen was contained in a smaller tube, 6 mm. diameter and 7·3 cm. long. This tube was used during the charging operation (see fig. 3). The pure palladium weighed 0·658 grm. This was placed in the tube, two glass-wool plugs being inserted as before, and the tube drawn out so as to form constrictions beyond the plugs. The charging was continued for 3 hours, and the palladium allowed to cool in the hydrogen for 2 hours. The tube was cut at the two constrictions, and a small dab of white wax immediately placed over the drawn-out open ends. This sealed tube was placed in the larger tube and suspended from the torsion arm at A. A series of readings was now made with the specimen in the double-walled phial (see Table II). Afterwards the phial was opened, and the palladium tube placed inside a wide tube, which was connected through a tube of gold wire with the manometer and Topler pump. The apparatus was then exhausted. By applying a small flame to the outer tube, the speck of wax was softened and the palladium tube opened to the vacuum. Afterwards the temperature of the palladium tube was raised to about 200° C. and the whole of the hydrogen pumped off.
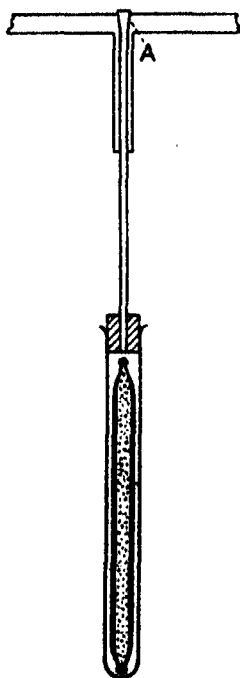
Fig. 4.

The volume of gas collected was 49 c.c. About 1 c.c. of this was unoccluded hydrogen, and therefore 0·66 grm. of palladium black contained 48 c.c. of hydrogen. Crystalline palladium has a density of 11·4, and, if the 0·66 grm. of palladium black were compressed to this density, its volume would be 0·06 c.c. nearly. This volume occludes 48 c.c. of hydrogen, and therefore one volume of crystalline palladium subjected to the same treatment would contain 48/0·06, or 800 c.c. of hydrogen.

When all the hydrogen had been pumped off, the palladium was allowed to cool in the vacuum. Air was next gently admitted, so as not to disturb the palladium, and a speck of wax again placed on the unsealed end of the tube. (It was found that the difference in weight between the tube, as originally sealed and as now sealed, was 0·026 grm., this being the excess of white wax in the former case over that in the latter. A subsidiary experiment showed that the wax was slightly paramagnetic, but the mass here involved would not affect the resulting deflection by more than one or two scale divisions, and, in any case, the difference due to this cause was

purposely made so as to give the slight increased deflection to the activated sample whose magnetic property, as indicated by the earlier determination, was less than that of pure palladium.)

The palladium tube was replaced in the phial and a series of readings taken as before (see Table II). During the above experiment it was observed that the active palladium preserved its metallic lustre, and when the tube containing it was rotated there was no adhesion of the particles to its walls, as was noticed in the previous specimens.

Calculation of the Susceptibilities of the Specimens.

From equation (1) the specific susceptibilities of the active and inactive palladium specimens are :—

$$\chi_{\text{inactive}} = +64 \cdot 6\,(7) \times 10^{-7},$$

$$\chi_{\text{active}} = \underbrace{36 \cdot 5 \times 10^{-7},\ 44 \cdot 6 \times 10^{-7}}_{24\ \text{hours},}\ \underbrace{48 \cdot 5 \times 10^{-7}}_{+14\ \text{hours}.}\ \text{after}$$

It appeared that the specific susceptibility was gradually returning to the value for the inactive specimen as the occluded hydrogen escaped through standing in contact with air. Fig. 5 shows the rate of recovery with time.[*]
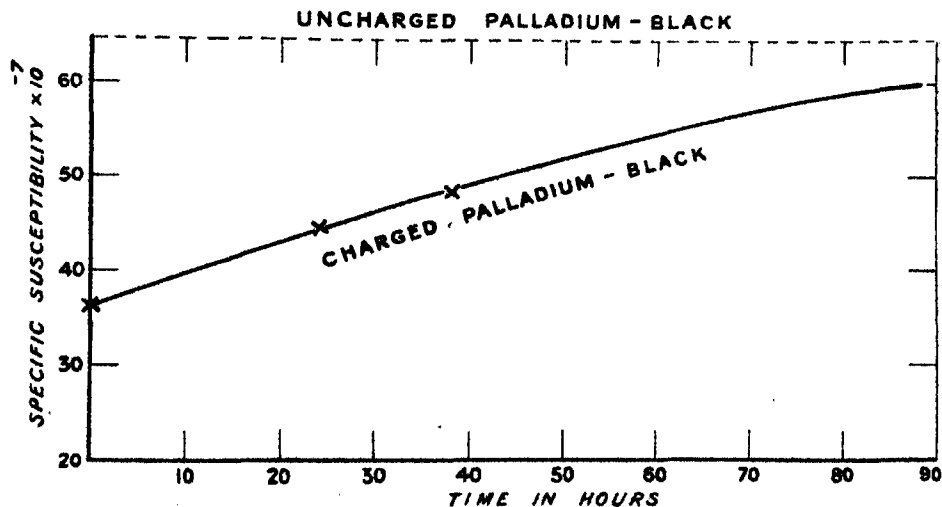
Fig. 5.

From the second series of experiments, the specific susceptibilities are :—

$$\chi_{\text{inactive}} = +64 \cdot 0 \times 10^{-7},$$

$$\chi_{\text{active}} = +53 \cdot 4 \times 10^{-7}, \qquad +51 \cdot 0 \times 10^{-7}.$$

[*] See footnote, p. 269.

The active specimen was again less paramagnetic than the inactive one by approximately 20 per cent., a value less than that obtained in the first series. The third and fourth series gave results of the same order as the second series.

The fifth series, as was to be expected, gave the greatest reduction, viz. :—

$$\chi_{\text{inactive}} = +64\cdot3 \times 10^{-7},^*$$

$$\chi_{\text{active}} = +14\cdot7 \times 10^{-7},$$

a reduction of 75 per cent.

3. Interpretation of the Experimental Results.

The hydrogen atom contains a single unbalanced electron, and, assuming that the nucleus, even if it rotates, contributes nothing to the magnetic properties, on account of its minute size, we should expect that *free* hydrogen atoms occluded in the palladium would involve an increase in the specific susceptibility. The experimental results described above therefore indicate that the hydrogen occluded by palladium is not in the *free* atomic state.

Molecular hydrogen, both in the gaseous and liquid state, is diamagnetic, and the existence of the occluded hydrogen in either of these states would therefore imply a smaller specific susceptibility for the active palladium. Such molecular hydrogen would not combine with the palladium. Therefore, knowing the specific susceptibility of hydrogen and the mass occluded, we can calculate the amount by which the specific susceptibility of the palladium would be reduced. Now, palladium of normal density 11·4 occludes 640 times its volume of hydrogen. Taking the mass of palladium black used in the earlier experiments as approximately 0·9 grm., and its volume as 1 c.c., the volume of hydrogen occluded by it should be of the order 70 c.c. The mass of this is 0·0063 grm. Taking the specific susceptibility of hydrogen as -30×10^{-7}, this occluded hydrogen would reduce the specific susceptibility of the palladium by $0\cdot19 \times 10^{-7}$, which is quite insufficient to account for the observed difference. Hence the occluded hydrogen is not *gaseous molecular* hydrogen or *condensed molecular* hydrogen in a state of mere solid solution or dissolved in the metal.

The magnetic property of a metallic compound is usually different from that of the components taken together. Thus iron and nickel are ferromagnetic, carbon monoxide is diamagnetic. The two carbonyls of iron and nickel, $Fe(CO)_5$ and $Ni(CO)_4$, are diamagnetic,† having susceptibilities com-

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* Honda, 'Ann. d. Phys.,' vol. 32, p. 1044 (1910), gives $+61\cdot2 \times 10^{-7}$, other values ranging down to $+58 \times 10^{-7}$ have been found.

† A. E. Oxley, 'Proc. Cam. Phil. Soc.,' vol. 16, p. 102 (1911).

parable with that of water. It is possible that something of this nature takes place when palladium occludes hydrogen. If a compound of palladium and hydrogen were formed which is diamagnetic or, at any rate, much less magnetic than pure palladium, the specific susceptibility of the hydrogen-palladium system might be reduced 50 per cent. or more below that of pure palladium.

One grm. of palladium contains 5.7×10^{21} atoms; 1 grm. of the palladium black, whose density is approximately 1, will occlude about 64 c.c. of hydrogen, which contains 3.4×10^{21} atoms of hydrogen. The ratio of the number of hydrogen atoms to the number of palladium atoms in 1 grm. of the palladium black is $3.4/5.7$ or 60 per cent. It is curious that the proportion of hydrogen atoms is a little greater than that of half the palladium atoms. We may perhaps suppose that a *loose* type of chemical compound is formed, loose because of the known great instability of the system and the readiness with which the occluded hydrogen is given off. Each hydrogen atom may be pictured as oscillating between two palladium atoms with which it is alternately in combination. The composition of the system would then correspond to that of the supposed compound Pd_2H, a view advocated by Troost, Hautefeuille, and by Wolf. It is possible for palladium to occlude still greater quantities of hydrogen, when the external pressure is increased, and in such cases there may be a tendency for a loose compound of the type PdH to form, or the excess hydrogen may form a solid solution in the system beyond this concentration.*

The magnetic results given in section (2) indicate a considerable drop in the susceptibility, varying from 70 per cent. in the fifth series, 40 per cent. in the first series, to 25 or 20 per cent. in the other series, and it is considered that the formation of an unstable compound or perhaps even a mere wandering of the hydrogen atom over the "surfaces" of the palladium atoms, to which the former temporarily attach themselves, is what actually occurs.

Now suppose that when a hydrogen atom is temporarily attached to a palladium atom the compound PdH formed is diamagnetic. At any moment only one-half the palladium atoms would show their normal magnetic property. Assuming a structure for the hydrogen atom like that suggested by the author† it is possible to picture the combination as shown in fig. 6, where the electron of the hydrogen atom has gone into the outer shell of electrons of the palladium atom. The PdH system would thus consist of two nuclei, those of normal palladium and hydrogen, with a system of electrons very similar to

* Ramsay, Mond and Shields, 'Phil. Trans.,' A, vol. 191, p. 105 (1898), indicate the possibility of the formation of a hydride Pd_3H_2 for large hydrogen contents.

† 'Roy. Soc. Proc.,' A, vol. 98, p. 264 (1921), and 'Nature,' vol. 105, p. 327 (1920).

that of silver, whose atomic number is one greater than palladium. Reasons have been given above for supposing that the magnetic property of elements
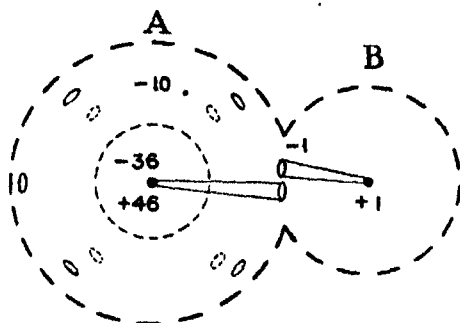
Fig. 6.

depends entirely on their electronic configuration, and therefore we should expect the temporary compound PdH to be, like silver, diamagnetic.

The specific susceptibity of silver is $-1\cdot86 \times 10^{-7}$, and, if half the electronic systems are similar to those of silver, their contribution to the magnetic property of 1 grm. of active palladium would be $-0\cdot93 \times 10^{-7}$, a quantity which is negligible compared with the susceptibility of palladium. Therefore the susceptibility of the palladium would be reduced by 50 per cent. As the occluded hydrogen escaped owing to mechanical disturbance, or combined with the oxygen of the air, the susceptibility would gradually rise until it reached the value for pure palladium (cf. fig. 5).

The electrical conductivity of palladium may be attributed to a tendency of the electrons in the outer shell of the atom to wander. It is conceivable that the attachment of a hydrogen atom in the manner indicated in fig. 6 would tend to counteract this, the hydrogen atom acting with regard to the nomad as a sort of anchor. Hence the electrical conductivity of the hydrogen-palladium system would fall off as the number of loose PdH units increased.[*] This agrees with Wolf's experiments.

The process of occlusion of hydrogen in crystalline palladium is a difficult one to understand. Holt and Andrew[†] have shown that if sufficient time is allowed, the capacity for occlusion is the same for crystalline and amorphous palladium. The atomic volume of palladium is not very different from that of hydrogen, and therefore the expansion of a palladium wire by about 15 per

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[*] Silver is a good conductor, and if its electron system is similar to that of Pd—H we must attribute the difference in the conductivities to the presence (externally) of the H nucleus in the Pd—H system.

[†] 'Roy. Soc. Proc.,' A, vol. 89, p. 170 (1913); A, vol. 90, p. 226 (1914).

cent., as observed by Graham,* the wire containing 600 times its own volume of hydrogen, is very small. It seems necessary to imagine that the crystalline lattice of palladium is hollow, like the diamond lattice.† If the hollowness is the determining factor in occlusion, this may throw some light on the atomic nature of the occluded gas, since molecules of hydrogen would not find a cavity large enough to accommodate them. It is important to note that the lattices of both palladium and silver are face-centred cubic. In the more open structures of the amorphous palladium, cavities must exist large enough to receive numbers of hydrogen molecules. Supposing these have entered, let us assume that there is an appreciable attraction between the Pd and H atoms which is comparable with that between two H atoms. Under this differential attraction and favourable collisions, a hydrogen molecule may be broken up and one hydrogen atom find itself in a hollow in the palladium lattice. This process may be repeated with the gradual diffusion of the hydrogen atoms through the palladium accompanied by the break up of the lattice. We know that diffusion of this kind does take place and we must assume that the thermal oscillations of the Pd atoms are sufficient to allow a way through for the hydrogen atoms eventually, though the process is very slow. The increased power of occlusion as the temperature of the palladium is raised to 100° C. is evidence of this. The expulsion of the hydrogen produced at 180° C. and above is due to oscillations of larger amplitude which permit the hydrogen atoms to unite and form molecules.

The experiments of Graham,‡ which indicate that *crystalline* palladium becomes more magnetic when charged with hydrogen, can be explained on the views expressed here.

His deduction of the existence of a magnetic " hydrogenium " is not in any way supported by more recent researches on the magnetic property of hydrogen in combination. Liquid§ and gaseous‖ hydrogen are diamagnetic, and atomic hydrogen¶ in all the hydrocarbons is diamagnetic. The free hydrogen atom is paramagnetic, but when it combines with a carbon atom the system is a compensated one. It is possible that each of the four hydrogen atoms in CH_4 holds a pair of electrons in common with the carbon atom. In the diamond, each of the four outer electrons of any atom is one of a pair of electrons held in common between two atoms, and recent X-ray evidence supports the view that weak diffraction centres exist half-way between the

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* ' Journ. Chem. Soc.,' vol. 22, p. 430 (1869).
† Sir William Bragg, ' Nature,' vol. 105, p. 79 (1921). (Abstract of Kelvin Lecture.)
‡ ' Journ. Chem. Soc.,' vol. 22, p. 430 (1869).
§ Onnes, ' Proc. Amsterdam Acad.,' vol. 14, p. 121 (1911).
‖ Soné, ' Science Reports, Tohoku,' vol. 8, p. 115 (1919).
¶ Pascal, ' Ann. de Chim. et de Phys.,' vol. 8, p. 19 (1910).

carbon nuclei in the diamond. In the amorphous variety this bonding of the carbon atoms is inappreciable ; the rigidity is small, but the power of occlusion large. May it not be that this capacity for occlusion is determined by a combination, similar to that which has been prescribed for the Pd—H system, the molecules of the occluded element first becoming dissociated, and finally sharing an electron with the carbon atom ? In the case of the diamond, where the electrons of the carbon atoms are already shared among themselves, occlusion would be impossible, even though there are hollows in the diamond lattice.

The two varieties of palladium are very similar in their behaviour to those of carbon. Amorphous carbon has a specific susceptibility $-20\cdot2 \times 10^{-7}$, diamond $-5\cdot0 \times 10^{-7}$, or four times smaller. The specific susceptibility of palladium black is 58×10^{-7}, crystalline palladium 11×10^{-7}, or five times smaller. Crystalline palladium, like diamond, is rigid, because its atoms are held together by electron sharing. The amorphous varieties have no cohesion, but high occlusion capacity. The greater the amount of amorphous palladium, the more rapidly will the hydrogen be occluded, and the expansion which results disintegrates the crystalline grains producing a larger amount of amorphous palladium. It is conceivable that circumstances may arise whereby, through internal strain, minute masses of the amorphous variety may be formed, which are screened off from attack by the hydrogen atoms by crystalline fragments through which the hydrogen diffuses very slowly. The heterogeneous system so formed would have a larger susceptibility than the original crystalline mass in proportion to the amount of such amorphous phase formed. When the hydrogen is driven off by heat, the palladium retracts, as Graham showed, and does so beyond its original dimensions, probably owing to the opportunity given to readjust internal strains which originally existed in the crystalline metal. Such retraction is often accompanied by a reduction of the occlusion capacity when the sample is again treated with hydrogen, and this is what might be expected. The properties of palladium in which the crystalline and amorphous phases co-exist are clearly complex, and a satisfactory solution can only be given when the relative proportions of these phases is determinate.

It has been suggested that, as regards the properties of the outer regions of the atom only, we may look upon any complex atom, e.g., a palladium atom, as consisting of an assemblage of hydrogen atoms.* If a free hydrogen atom

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* A. E. Oxley, 'Nature,' vol. 105, p. 327 (1920). Any negative charges necessary to cement the positive charges of the nucleus are not involved here The disintegration of a hydrogen nucleus would depend on the attraction between it and the nuclear electrons ; once this had taken place, e.g., by bombardment with α-particles (cf. Rutherford, 'Phil. Mag.,' vol. 41, p. 513 (1920)), the H-nucleus would take up an electron and become a neutral H-atom.

attaches itself to such a system as shown in fig. 6, a considerable amount of heat would be evolved. For two hydrogen atoms combining, the thermal evolution is 77,000 calories per gramme.* Mond, Ramsay, and Shields have shown that the heat set free when 1 grm. of hydrogen is occluded in palladium is 6,472 calories. The thermal value of the combination of palladium and hydrogen will be the sum of these numbers, or 83,500 calories per gramme of combined hydrogen. This implies that the Pd—H system, in the absence of excess hydrogen, is exceedingly stable. The presence of other hydrogen atoms, or oxygen (if the system is in contact with air), will make the Pd—H system less stable, and measurable in fact by the thermal change 6,472 calories per gramme of hydrogen, as determined by Mond, Ramsay, and Shields. The view which has often been put forward that the hydrogen is merely condensed as a liquid within the metal, not only gives the low thermal change of 123 calories for the occlusion of 1 grm. of hydrogen, but demands the presence of very stable hydrogen molecules which are inconsistent with the great activity of the hydrogen-palladium system.

4. Theoretical Application of the Above Results to Other Systems.

The formation of an electronic system corresponding to an element of higher atomic number than that of the occluding element, such as those of the palladium-hydrogen and silver systems described above, is suggestive in connection with the change of magnetic properties of other elements containing occluded hydrogen. It has been shown that pure manganese is paramagnetic, its specific susceptibility at 18° C. being $+11 \times 10^{-6}$. When manganese is fused in an atmosphere of hydrogen, or is deposited electrolytically, it is ferro-magnetic, the highest values of χ being of the order $+2000 \times 10^{-6}$. Such manganese contains a certain amount of occluded hydrogen, the abstraction of which causes the manganese to assume its normal paramagnetic susceptibility.[†]

Now, the atomic number of manganese is 25, that of iron 26. If we suppose that, when hydrogen is occluded in manganese, the electron of the hydrogen atom enters into the outer shell of the manganese atom, an electronic system similar to that of iron would result. As before, the Mn—H system differs from the Fe system, since the former has two nuclei, one of manganese the other of hydrogen, while the latter has the single iron nucleus. We might expect, therefore, that the presence of hydrogen in manganese would tend a make a certain number of the manganese atoms

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* Langmuir, ' Phil. Mag.,' vol. 27, p. 188 (1914).

† Hadfield, Chéneveau and Geneau, ' Roy. Soc. Proc.,' A, vol. 94, p. 69 (1917) ; also Weiss and Onnes, ' Comptes Rendus,' vol. 150, p. 686 (1910).

ferro-magnetic, in proportion to the number of hydrogen atoms occluded in the manganese.

We can calculate the amount of hydrogen which would be necessary to produce the rise of susceptibility referred to above. The saturation moment of 1 grm.-atom of iron is 11×1123,[*] and the magnetic moment of each atom $11 \times 1123/6\cdot06 \times 10^{23}$. Suppose that the hydrogen atoms in 1 grm. of manganese are effective in producing N electronic systems similar to that of the iron atom. The magnetic moment of these will be

$$N \times 11 \times 1123/6\cdot06 \times 10^{23}.$$

The rise of susceptibility of the manganese is from $11\cdot0 \times 10^{-6}$ to 2200×10^{-6}, or 2189×10^{-6}, for a field strength of 320[†] gauss. This implies an increase of magnetic moment of $2189 \times 10^{-6} \times 320$ per gramme. Hence

$$N = 2189 \times 10^{-6} \times 320 \times 6\cdot06 \times 10^{23}/1123 \times 11 = 3\cdot2 \times 10^{19}.$$

This is the number of Mn—H systems present, and is also equal to the number of H atoms per *gramme* of manganese necessary to produce the ferro-magnetism in the manganese. The mass of this hydrogen is $3\cdot2 \times 10^{19}/6\cdot06 \times 10^{23}$, or $5\cdot4 \times 10^{-5}$ grm., and its volume nearly $0\cdot6$ c.c. per gramme of manganese. The density of manganese is $7\cdot5$, and therefore, according to this calculation, this element would occlude $4\cdot5$ times its own volume of hydrogen. This is a reasonable estimate compared with the capacities for occlusion of other elements[‡] :—

	Vols.			Vols.
Palladium black	502		Nickel	17·6
Platinum sponge	49·3		Copper	4·5
Gold	46·3		Aluminium	2·7
Iron	19·2		Lead	0·15

In soft iron the coercive force is about 2 and sometimes less; that of cobalt may reach a value as high as 12.[§] The fact that iron which has been fused in an atmosphere of hydrogen has a larger coercive force than 2

* Weiss, 'Archives des Sciences Phys. et Nat.,' vol. 31 (1911).

† Hadfield, Chéneveau and Geneau, *loc. cit.*, p. 70, footnote.

[*Note added, January* 8, 1922.—The amount of hydrogen in this specimen was not measured, but Sir Robert Hadfield informs me that in a sample of electrolytic manganese, 45 c.c. of hydrogen were driven off per cubic centimetre of manganese. Kuh ('Thèse,' Zurich, 1911) has obtained a magnetic moment for ferromagnetic manganese twice as large as that recorded above, and this would correspond to 9 c.c. of occluded hydrogen per cubic centimetre of manganese. These calculated values are not so large as the experimental value recorded above, but it should be borne in mind that the *isolated* Mn—H systems have been assumed to be identical with *contiguous* Fe atoms, and the difference is possibly due to this.]

‡ Neumann and Strientz, 'Monatshefte f. Chemie,' vol. 13, p. 40 (1892); vol. 12, p. 642 (1891).

§ Ewing, 'Magnetic Induction in Iron and Other Metals,' pp. 83–86.

is suggestive. In this case it is conceivable that the occluded hydrogen atoms thrust their electrons into the outer shells of the iron atoms, and produce a combined electronic system analogous to that of cobalt.

On the cubical atom theory of Lewis and Langmuir, some insight as to the relation between magnetic property and structure of the elements may be obtained which are not inconsistent with the views expressed above. Langmuir points out that "The properties of the atoms are determined by the number and arrangement of electrons in the outside layer and the ease with which they are able to revert to more stable forms by giving up or taking up electrons, or by sharing their outside electrons with atoms with which they combine. The tendencies to revert to the forms represented by the atoms of the inert gases are the strongest, but there are a few other forms of high symmetry, such as those corresponding to certain possible forms of nickel, palladium, erbium, and platinum atoms, towards which atoms have a weaker tendency to revert (by giving up electrons only)."

According to Lewis, the most stable electron arrangement is that of the pair, and, as regards the formation of compounds, Langmuir remarks : " The pair of electrons in the helium atom represents the most stable possible arrangement. A stable pair of this kind forms only under the direct influence of positive charges. The positive charges producing the stable pair may be :—

" (*a*) The nucleus of any element.

" (*b*) Two hydrogen nuclei.

" (*c*) A hydrogen nucleus together with the kernel of an atom.

" (*d*) Two atomic kernels.

" These are listed in the order of their stability."

(*a*) represents the helium atom ; (*b*) the hydrogen molecule ; (*c*) the systems Pd—H, Mn—H, Fe—H, Pt—H, etc.; (*d*) the more complex ferro-magnetic systems Mn—B, Mn—P, Mn—As, etc., and the Heusler alloys. In cases (*c*) and (*d*) where one or both of the atoms have complex structure, the electrons arrange themselves in octets, which may be very much distorted. Octets may hold electrons in common with other octets, but such electrons must form one, two, or three pairs. When electrons are held in common no ionisation of the atoms takes place, and in such cases the especially close relationship between the electrons forming the pair have suggested an electro-magnetic origin of the coupling force between the atoms.* Where the chemical affinity is small, or is a differential one, as is probably the case in the unstable compounds formed during occlusion, the tendency will be for the atoms to satisfy their needs by sharing electrons.

* A. E. Oxley, ' Roy. Soc. Proc.,' A, vol. 98, p. 264 (1921).

The Cause of Encke's Division in Saturn's Ring.

By G. R. GOLDSBROUGH, D.Sc., Armstrong College, Newcastle-on-Tyne.

§ 1. *Introductory.*

In a former paper,* the effect of satellites in producing divisions in Saturn's Rings was discussed. The case taken was that where the satellite orbit and the rings were co-planar. The results afforded an explanation of the outer dimension of the Ring, Cassini's Division, the inner radius of the bright ring, and the existence of the Crêpe Ring. But no reason was given for the existence of Encke's Division, nor the numerous divisions reported by Lowell. In carrying the examination further, the fact that the satellite orbits are not precisely co-planar with the ring system must be considered. As given by the 'Annuaire du Bureau des Longitudes,' the inclination of the plane of the rings to the ecliptic is 28° 5·6′, while the corresponding inclinations of the satellite orbits are—

Mimas	27° 29·6′,	Dione	28° 4·4′,
Enceladus	28° 4·3′,	Rhea	28° 22·8′,
Tethys	28° 40·5′,	Titan	27° 39·7′.

In the cases of Mimas, Tethys, and Titan, the differences are distinctly marked, the first being 36′, or 0·01 of a radian. The effect of this inclination is examined in the sequel.

The general hypotheses are the same as in the former paper, to which the reader is referred.

§ 2. *The Equations of Motion.*

Using the same notation as in the former paper, let M be the mass of the primary supposed situated at the origin of co-ordinates. It is surrounded by a single ring of p particles, whose unperturbed positions are in the xy plane, at the corners of a regular polygon. We shall take the co-ordinates of one of these particles, m_λ, as x_λ, y_λ, z_λ, or r_λ, θ_λ, z_λ; r and θ being measured in the xy plane. The unperturbed values of these co-ordinates will be $z_\lambda = 0$, $r_\lambda = a$, $\theta_\lambda = \omega t + \epsilon + \lambda 2\pi/p$, where $\omega^2 a^3 = M + m_\lambda = M$.

The perturbing satellite, of mass m', describes a circular orbit of radius a' in a plane inclined at an angle γ to the xy plane. Any ellipticity of the primary M is neglected, so that the orbit of m' has stationary nodes. It

* 'Phil. Trans.,' A, vol. 222, p. 101.

has been shown by Stroobant,[*] that Saturn's Ring, as a whole, has little effect upon the movements of the satellites. We are therefore justified in treating the orbit of m' as an unperturbed circle. The co-ordinates of m' at time t will be

$$x' = a' \cos \theta', \quad y' = a' \sin \theta' \cos \gamma, \quad z' = a' \sin \theta' \sin \gamma,$$

where
$$\theta' = \omega' t + \epsilon',$$

and
$$\omega'^2 a'^3 = M + m' = M.$$

We have here taken the line of nodes as the x-axis, and have measured θ' in the plane of the orbit.

The equations of motion are now, for the particle m_λ

$$
\left.
\begin{aligned}
\ddot{r}_\lambda - r_\lambda \dot{\theta}_\lambda^2 &= \frac{\partial F}{\partial r_\lambda}, \\
\frac{1}{r_\lambda} \frac{d}{dt} (r_\lambda^2 \theta_\lambda) &= \frac{1}{r_\lambda} \frac{\partial F}{\partial \theta_\lambda}, \\
\ddot{z} &= \frac{\partial F}{\partial z_\lambda}.
\end{aligned}
\right\}
\tag{1}
$$

In these

$$F \equiv \frac{M + m_\lambda}{(r_\lambda^2 + z_\lambda^2)^{1/2}} + \frac{m'}{\Delta_\lambda} - \frac{m'}{a'^3} (x_\lambda x' + y_\lambda y' + z_\lambda z')$$

$$+ \sum_\mu \frac{m_\mu}{D_{\lambda\mu}} - \sum_\mu \frac{m_\mu (x_\lambda x_\mu + y_\lambda y_\mu + z_\lambda z_\mu)}{(r_\mu^2 + z_\mu^2)^{3/2}},$$

where
$$\Delta_\lambda^2 = (x_\lambda - x')^2 + (y_\lambda - y')^2 + (z_\lambda - z')^2,$$

and
$$D_{\lambda\mu}^2 = (x_\lambda - x_\mu)^2 + (y_\lambda - y_\mu)^2 + (z_\lambda - z_\mu)^2$$
$$= r_\lambda^2 + r_\mu^2 - 2 r_\lambda r_\mu \cos(\theta_\lambda - \theta_\mu) + (z_\lambda - z_\mu)^2.$$

In the case of Saturn's Rings, the particles forming any ring can only perform small vibrations in the plane of the ring about their zero positions if collision with other particles is to be avoided. We therefore assume

$$r_\lambda = a(1 + \rho_\lambda),$$

and
$$\theta_\lambda = \omega t + \epsilon + \lambda 2\pi / p + \sigma_\lambda,$$

where ρ_λ and σ_λ are small.

When the orbit of the perturbing satellite is in the xy plane, $z_\lambda = 0$ is a solution of the equations (1). Further, as we shall only consider the case where the inclination of the satellite orbit is small (and therefore we may replace $\sin \gamma$ by γ and $\cos \gamma$ by unity), we assume

$$z_\lambda = a\gamma \zeta_\lambda,$$

ζ_λ being also small.

[*] 'Comptes Rendus,' vol. 172, p. 913.

The equations (1) now become

$$a\ddot{p}_\lambda - 2a\omega\dot{\sigma}_\lambda - \omega^2\rho_\lambda - a\omega^2 = \left(\frac{\partial F}{\partial r_\lambda}\right)_0 + \Sigma_\mu a\rho_\mu \left(\frac{\partial^2 F}{\partial r_\lambda \partial r_\mu}\right)_0$$

$$+ \Sigma_\mu \sigma_\mu \left(\frac{\partial^2 F}{\partial r_\lambda \partial \theta_\mu}\right)_0 + \Sigma_\mu a\gamma\zeta_\mu \left(\frac{\partial^2 F}{\partial r_\lambda \partial z_\mu}\right)_0,$$

$$a\ddot{\sigma}_\lambda + 2\omega a\dot{p}_\lambda = \left(\frac{\partial F}{r_\lambda \partial \theta_\lambda}\right)_0 + \Sigma_\mu a\rho_\mu \left(\frac{\partial^2 F}{\partial r_\mu . \, r_\lambda \partial \theta_\lambda}\right)_0$$

$$+ \Sigma_\mu \sigma_\mu \left(\frac{\partial^2 F}{\partial \theta_\mu . \, r_\lambda \partial \theta_\lambda}\right)_0 + \Sigma_\mu a\gamma\zeta_\mu \left(\frac{\partial^2 F}{\partial z_\mu . \, r_\lambda \partial \theta_\lambda}\right)_0,$$

$$a\gamma\ddot{\zeta}_\lambda = \left(\frac{\partial F}{\partial z_\lambda}\right)_0 + \Sigma_\mu a\rho_\mu \left(\frac{\partial^2 F}{\partial r_\mu \partial z_\lambda}\right)_0$$

$$+ \Sigma_\mu \sigma_\mu \left(\frac{\partial^2 F}{\partial \theta_\mu \partial z_\lambda}\right)_0 + \Sigma_\mu a\gamma\zeta_\mu \left(\frac{\partial^2 F}{\partial z_\mu \partial z_\lambda}\right)_0. \quad\quad (2)$$

Now

$$\Delta_\lambda^2 = r_\lambda^2 + z_\lambda^2 + a'^2 - 2r_\lambda a' \{\cos\theta_\lambda \cos\theta' + \sin\theta_\lambda \sin\theta' \cos\gamma\} - 2z_\lambda z'.$$

Since $\cos\gamma$ is replaced by unity, and in the formation of zero values of the derivatives we put $z_\lambda = 0$, it is clear that, wherever it appears in the equations (2), Δ_λ has the same value as in the equations of the former paper.

In the same way the other zero values are

$$D_{\lambda\mu}^2 = 4a^2 \sin^2(\lambda - \mu)\pi/p,$$

$$x_\lambda x' + y_\lambda y' + z_\lambda z' = aa' \cos(\omega't + \epsilon' - \omega t - \epsilon - \lambda 2\pi/p),$$

and

$$x_\lambda x_\mu + y_\lambda y_\mu + z_\lambda z_\mu = a^2 \cos(\lambda - \mu) 2\pi/p.$$

It is evident, then, that the terms of equations (2) will all be the same as those of the former paper except where z-derivatives appear. The latter terms are now evaluated:—

$$\Sigma_\mu a\gamma\zeta_\mu \left(\frac{\partial^2 F}{\partial z_\mu \partial r_\lambda}\right)_0 = -\frac{3m' aa'}{\Delta_\lambda^5} \gamma^2 \{a - a' \cos(\theta' - \theta_\lambda)\} \sin\theta' \zeta_\lambda$$

$$= 0, \text{ to the order of value we are using.}$$

$$\Sigma_\mu a\gamma\zeta_\mu \left(\frac{\partial^2 F}{\partial z_\mu . \, r_\lambda \partial \theta_\lambda}\right)_0 = \frac{3m' aa'^2 \gamma^2 \sin\theta'}{\Delta_\lambda^5} \sin(\theta' - \theta_\lambda) \zeta_\lambda$$

$$= 0,$$

$$\left(\frac{\partial F}{\partial z_\lambda}\right)_0 = m' \sin\theta' . \gamma \left\{\frac{a'}{\Delta_\lambda^3} - \frac{1}{a'^2} + \frac{3a}{a'^3}\cos(\theta' - \theta_\lambda)\right\},$$

$$\Sigma_\mu a\rho_\mu \left(\frac{\partial^2 F}{\partial z_\lambda \partial r_\mu}\right)_0 = 3m' a\gamma\rho_\lambda \sin\theta' \left\{-\frac{aa' - a'^2\cos(\theta' - \theta_\lambda)}{\Delta_\lambda^5} + \frac{a}{a'^4}\cos(\theta' - \theta_\lambda)\right\},$$

$$\Sigma_\mu \sigma_\mu \left(\frac{\partial^2 F}{\partial \theta_\mu \partial z_\lambda}\right)_0 = 3m' a\gamma\sigma_\lambda \sin\theta' \left\{\frac{a'^2}{\Delta_\lambda^5}\sin(\theta' - \theta_\lambda) + \frac{1}{a'^3}\sin(\theta' - \theta_\lambda)\right\},$$

$$\Sigma_\mu a\gamma\zeta_\mu \left(\frac{\partial^2 F}{\partial z_\mu \partial z_\lambda}\right)_0 = \left[-\frac{M + m_\lambda}{a^3} - \frac{m'}{\Delta_\lambda^3} - \Sigma_\mu \frac{m_\mu}{D_{\lambda\mu}^3}\right] a\gamma\zeta_\lambda + \Sigma_\mu \frac{m_\mu}{D_{\lambda\mu}^3}\zeta_\mu.$$

In the last expression the μ-summation in the right-hand member does not include the case $\mu = \lambda$. Also θ' now equals $\omega't + \epsilon'$ and θ_λ equals $\omega t + \epsilon + \lambda 2\pi/p$.

It is clear from these results that the first pair of equations (2) remain unchanged by the small inclination of the satellite orbit. The effect of this inclination is only to produce vibrations normal to the plane of the ring.

We are therefore left with the single set of equations

$$\ddot{\zeta}_\lambda = m' \sin \theta' \left\{ \frac{a'}{a\Delta_\lambda{}^3} - \frac{1}{aa'^2} + \frac{3}{a'^3} \cos (\theta' - \theta_\lambda) \right\}$$

$$+ 3m' \sin \theta' \left\{ -\frac{aa' - a'^2 \cos (\theta' - \theta_\lambda)}{\Delta_\lambda{}^5} + \frac{a}{a'^4} \cos (\theta' - \theta_\lambda) \right\} \rho_\lambda$$

$$+ 3m' \sin \theta' \left\{ \frac{a'^2}{\Delta_\lambda{}^5} \sin (\theta' - \theta_\lambda) + \frac{1}{a'^3} \sin (\theta' - \theta_\lambda) \right\} \sigma_\lambda$$

$$+ \left\{ -\frac{M + m_\lambda}{a^3} - \frac{m'}{\Delta_\lambda{}^3} - \sum_\mu \frac{m_\mu}{D_{\lambda\mu}{}^3} \right\} \zeta_\lambda + \sum_\mu \frac{m_\mu}{D_{\lambda\mu}{}^3} \zeta_\mu. \tag{3}$$

It is to be noted that this equation holds for all integral values of λ from 1 to p. It is independent of γ; and the quantities ρ_λ, σ_λ are known for all values of λ, having been determined from the first two of equations (1) which have been solved to the necessary degree of approximation previously.

In the former paper, certain approximations were made to render possible the solution of the period equation without a definite knowledge of the separate masses forming a ring.[*] This approximation amounted to the use of the mean position instead of the actual position of a particle in calculating its perturbing effect upon another particle. If we adopt the same process again, we reject the terms $\sum_\mu \frac{m_\mu}{D_{\lambda\mu}{}^3} \zeta_\mu$ in equation (3). We have then a series of p equations for the motion of the p particles, each equation containing the co-ordinates of the particle under consideration and not the co-ordinates of the other particles. This of course very much simplifies the work.

We may write

$$\Delta_\lambda{}^{-3} = a'^{-3} \sum_i c_i \cos i (\theta' - \theta_\lambda),$$

$$\Delta_\lambda{}^{-5} = a'^{-5} \sum_i d_i \cos i (\theta' - \theta_\lambda).$$

On substituting these and reducing the expressions, we find that equations (3) may be written

$$\ddot{\zeta}_\lambda + \zeta_\lambda \sum_j \Phi_{1,j} \cos j (\theta' - \theta_\lambda) + \rho_\lambda \sum_j \Phi_{2,j} \sin \{(j+1) \theta' - j \theta_\lambda\}$$

$$+ \sigma_\lambda \sum_j \Phi_{3,j} \cos \{(j+1) \theta' - j \theta_\lambda\} = \sum_j \Phi_{4,j} \sin \{(j+1) \theta' - j \theta_\lambda\}. \tag{4}$$

[*] *Loc. cit.*, pp. 123 and 124.

In these equations the values of the coefficients Φ are readily obtained. In particular

$$\Phi_{1,0} = \omega^2 + \omega^2 \sum_{\mu} \frac{m_{\mu}}{M} \frac{1}{\sin^3 (\lambda - \mu) \pi / p} + \nu' \omega'^2 c_0.$$

As was shown in the previous paper,[*] $\sum_{\mu} \dfrac{m_{\mu}}{M} \dfrac{1}{8 \sin^3 (\lambda - \mu) \pi / p}$ ranges in value from zero to $0.0096 \, p^3 \bar{m} / M$, where $\bar{m}$ is the maximum mass of a particle appearing in the ring. All the quantities Φ except $\Phi_{1,0}$ are factored by ν' or m'/M. As this quantity is very small, all the quantities Φ except $\Phi_{1,0}$ will be small, and their squares and products may be neglected. Also in $\Phi_{1,0}$ the term $\nu' \omega'^2 c_0$ may be rejected in comparison with the other two. We shall then write

$$\Phi_{1,0} = \omega^2 + \omega^2 F_{\lambda}.$$

§ 3. The Solution of the Equations.

In solving equations (4) let us first take the complementary function. The equation to be solved is

$$\ddot{\zeta} + \zeta \left[\sum_{j} \Phi_{1,j} \cos j (\omega' t + \epsilon' - \omega t - \epsilon - \lambda 2 \pi / p) \right] = 0. \qquad (5)$$

The solutions of the system are obtained by giving to λ its p values $1, 2, \ldots p$. The equation is of Hill's well-known form and can readily be solved by the method of Whittaker and Ince.[†] To simplify the form, change the independent variable from t to ϕ which equals $\omega' t + \epsilon' - \omega t - \epsilon - \lambda 2 \pi / p$. Then

$$\zeta'' + \zeta \left[\frac{1}{(\omega' - \omega)^2} \sum_{j} \Phi_{1,j} \cos j \phi \right] = 0. \qquad (6)$$

Let $\zeta = e^{c\phi} u$, where u is a periodic function of the independent variable ϕ. Then

$$c^2 u + 2 c u' + u'' + u \left[\frac{1}{(\omega' - \omega)^2} \sum \Phi_{1,j} \cos j \phi \right] = 0. \qquad (7)$$

Also let

$$u = \cos (n\phi - \tau) + \sum_{i} P_i \Phi_{1,i} \ldots ,$$

$$c = \qquad\qquad \sum_{i} Q_i \Phi_{1,i} \ldots ,$$

$$\Phi_{1,0} = n^2 (\omega' - \omega)^2 + \sum R_i \Phi_{1,i} \ldots .$$

In the summations, all integral values of i are to be taken except $i = 0$. The general case should include products of the quantities Φ, but as has been pointed out these may be neglected. The quantities Q_i and R_i are constants,

* P. 123.

† 'Monthly Notices, R.A.S.,' LXXV, 5, p. 436.

and P_i is a periodic function of ϕ. If we add the two conditions: (1) That no term $\sin(n\phi - \tau)$ may appear in the expression for u, and (2) that u is purely periodic, we are able to determine completely all the coefficients entering into the expressions.

On substituting in equations (7) and equating to zero the coefficients of those terms which are independent of Φ, we have an identity. From the coefficient of $\Phi_{1, i}$ we find

$$- 2n \, Q_i \sin(n\phi - \tau) + P_i'' + n^2 P_i + \frac{R_i}{(\omega' - \omega)^2} \cos(n\phi - \tau)$$
$$+ \frac{\cos(n\phi - \tau) \cos i\phi}{(\omega' - \omega)^2} = 0. \quad (8)$$

In general, therefore,
$$Q_i = 0, \qquad R_i = 0,$$
$$P_i = \frac{\frac{1}{2} \cos\{(i + n)\phi - \tau\}}{(\omega' - \omega)^2 \{(i + n)^2 - n^2\}} + \frac{\frac{1}{2} \cos\{(i - n)\phi - \tau\}}{(\omega' - \omega)^2 \{(i - n)^2 - n^2\}}. \quad (9)$$

But in the particular case of $i = 2n$, equation (8) reduces to

$$- 2n \, Q_{2n} \sin(n\phi - \tau) + P_{2n}'' + n^2 P_{2n} + \frac{R_{2n}}{(\omega' - \omega)^2} \cos(n\phi - \tau)$$

$$+ \frac{1}{(\omega' - \omega)^2} \{ \tfrac{1}{2} \cos(3n\phi - \tau) + \tfrac{1}{2} \cos(n\phi - \tau) \cos 2\tau - \tfrac{1}{2} \sin(n\phi - \tau) \sin 2\tau \} = 0.$$

Whence, to fulfil the given conditions,

$$Q_{2n} = - \frac{\sin 2\tau}{4n(\omega' - \omega)^2},$$
$$R_{2n} = - \tfrac{1}{2} \cos 2\tau,$$
$$P_{2n} = \frac{\cos(3n\phi - \tau)}{16 n^2 (\omega' - \omega)^2}. \quad (10)$$

We have, then,
$$c = - \frac{\sin 2\tau}{4n(\omega' - \omega)^2} \, \Phi_{1, \, 2n},$$
and
$$\Phi_{1, \, 0} = n^2 (\omega' - \omega)^2 - \tfrac{1}{2} \Phi_{1, \, 2n} \cos 2\tau. \quad (11)$$

These two expressions, together with (9) and (10), constitute a solution valid in the vicinity of $\Phi_{1, \, 0} = n^2 (\omega' - \omega)^2$, where n is any integer. The parameter τ is determined from the second of equations (11). The value so obtained, substituted in the expression for c, determines that quantity completely. It is clear that real values of τ mean real values of c, and hence vibrations of increasing amplitude or instability. Real values of τ can only occur when

$$| \Phi_{1, \, 0} - n^2 (\omega' - \omega)^2 | \geqq | \tfrac{1}{2} \Phi_{1, \, 2n} | \, ;$$

and owing to the extreme smallness of $\Phi_{1, 2m}$, this is, with a close degree of approximation, when

$$\Phi_{1, 0} - n^2 (\omega' - \omega)^2 \lesseqgtr 0. \tag{12}$$

We pass next to the particular integral of equation (4). The values of ρ_λ and σ_λ to be used are obtained from the former paper. From p. 110, we have

$$\rho = e^{c\phi} \{ A_0 \sin (n\phi - \tau) + \Sigma\Sigma A_{r, s} \Theta_{r, s} \dots \},$$

and

$$\sigma = e^{c\phi} \{ X_0 \cos (n\phi - \tau) + \Sigma\Sigma X_{r, s} \Theta_{r, s} \dots \}.$$

In these expressions A_0 and X_0 are related constants, and $A_{r, s}$, $X_{r, s}$ are determined later in the paper. As, however $\Theta_{r, s}$ is of the same order as $\Phi_{2, j}$ and $\Phi_{3, j}$, it is evident that on substituting in equation (4) only the first terms of the expressions for ρ and σ need be used. We have further to add the particular integrals for ρ and σ given on p. 117 of the former paper. As again, these particular integrals are of the same order of value as the quantities $\Phi_{2, j}$ and $\Phi_{3, j}$ it is clear that we may omit them in making the substitutions. The final result is that the values of ρ and σ will both produce terms of the type

$$\Omega_i \cos \{ (i + 1) \theta' - i\theta_\lambda \} \ . \ \exp. c (\theta' - \theta_\lambda),$$

where i may take all integral values, positive and negative, and c and Ω_i are known constants of the same order as $\Phi_{2, j}$ and $\Phi_{3, j}$.

Particular integrals will arise from these terms and also from the remaining terms

$$\Phi_{4, j} \sin \{ (j + 1) \theta' - j\theta_\lambda \}.$$

Taking the first of these we have to find the particular integral of

$$\ddot{\zeta}_\lambda + \zeta_\lambda \sum_j \Phi_{1, j} \cos j (\theta' - \theta_\lambda) = \Omega_i \cos \{ (i + 1) \theta' - i\theta_\lambda \} \exp. c (\theta' - \theta_\lambda). \tag{13}$$

Removing $\exp. \{ c (\theta' - \theta_\lambda) \}$, and neglecting c^2, we have

$$2c (\omega' - \omega) \dot{\zeta}_\lambda + \ddot{\zeta}_\lambda + \zeta_\lambda \sum_j \Phi_{1, j} \cos j (\theta' - \theta_\lambda) = \Omega_i \cos \{ (i + 1) \theta' - i\theta_\lambda \}.$$

On working out the particular integral in the way previously adopted,[*] and noting that products of Φ and Ω may be rejected, we have

$$\zeta_\lambda = \frac{\exp. \{ c (\theta' - \theta_\lambda) \} \Omega_i}{\Phi_{1, 0} - \{ (i + 1) \omega' - i\omega \}^2} \left\{ \cos \{ (i + 1) \theta' - i\theta_\lambda \} \right.$$

$$\left. + \frac{2c (\omega' - \omega) \{ (i + 1) \omega' - i\omega \}}{\Phi_{1, 0} - \{ (i + 1) \omega' - i\omega \}^2} \sin \{ (i + 1) \theta' - i\theta_\lambda \} \right\},$$

or, to the same order of values, rejecting the product $c\Omega_i$,

$$\zeta_\lambda = \frac{\exp. \{ c (\theta' - \theta_\lambda) \} \Omega_i}{\Phi_{1, 0} - \{ (i + 1) \omega' - i\omega \}^2} \cos \{ (i + 1) \theta' - i\theta_\lambda \}. \tag{14}$$

* *Loc. cit.*, p. 116.

To this must be added the particular integral of

$$\zeta_\lambda + \zeta_\lambda \Sigma_j \Phi_{1,j} \cos j(\theta' - \theta_\lambda) = \Phi_{4,j} \sin\{(j+1)\theta' - j\theta_\lambda\}. \qquad (15)$$

To the same order of approximation, the required integral is

$$\zeta_\lambda = \frac{\Phi_{4,j} \sin\{(j+1)\theta' - j\theta_\lambda\}}{\Phi_{1,0} - \{(j+1)\omega' - j\omega\}^2}. \qquad (16)$$

Finally, the whole particular integral is represented by the sum of (14) and (16).

§ 4. *Discussion of the Results.*

Expression (12), with the meaning of $\Phi_{1,0}$ inserted, is

$$\omega^2 + \omega^2 F_\lambda = n^2(\omega' - \omega)^2. \qquad (17)$$

As already pointed out, for the differing values of λ, F_λ ranges from zero to $0\cdot0096\, p^3\bar{m}/M$. As in the previous paper, we shall treat F_λ as a parameter varying continuously between the limits mentioned. Solving (17) and taking only the case where $\omega > \omega'$,

$$\frac{\omega'}{\omega} = \frac{n - \sqrt{(1+F_\lambda)}}{n}. \qquad (18)$$

The maximum value of F_λ as determined from the observed dimensions of Cassini's Division is $0\cdot0173$. The following Table gives the positions of the divisions resulting from the instability :—

	$F_\lambda = 0.$		$F_\lambda = 0\cdot0173.$	
	$\omega'/\omega.$	$a/a'.$	$\omega'/\omega.$	$a/a'.$
$n = 1$	0	0	—	—
2	$\frac{1}{2}$	$0\cdot630$	$0\cdot4958$	$0\cdot626$
3	$\frac{2}{3}$	$0\cdot763$	$0\cdot6639$	$0\cdot761$

Applying these results to the case of satellite Mimas, we should find, from the solution $n = 2$, a narrow division in Saturn's Ring extending from $16\cdot9''$ to $16\cdot8''$. This is just at the inner edge of Cassini's Division. For Enceladus the same solution would give a narrow division from $21\cdot7''$ to $21\cdot6''$. This is outside the limits of the existing ring. The solution for $n = 3$ gives for Mimas a narrow division at $20\cdot5''$. This is again just outside the existing ring.

The normal vibrations represented by the solution (17) do not lead, then, to any new divisions in the Ring of Saturn. The particular integral, represented by the sum of (14) and (16), becomes large, and instability ensues in the vicinity of that position where

$$\Phi_{1,0} - \{(i+1)\omega' - i\omega\}^2 = 0. \qquad (19)$$

Taking the value of $\Phi_{1,0}$, equation (19) becomes

$$\omega^2(1+F_\lambda)-\{(i+1)\,\omega'-i\omega\}^2 = 0.$$

The solution of this equation for which $\omega > \omega'$ is

$$\frac{\omega'}{\omega} = \frac{i-\sqrt{(1+F_\lambda)}}{i+1}. \qquad (20)$$

As before, F_λ ranges in value from 0 to 0·0173. The following Table gives the limits of the zones of instability arising from (20) for various values of i, which is an integer :—

	$F_\lambda = 0.$		$F_\lambda = 0·0173.$	
	$\omega'/\omega.$	$a/a'.$	$\omega'/\omega.$	$a/a'.$
$i = 1$	0	0	—	—
2	¼	0·481	0·381	0·478
3	⅓	0·630	0·498	0·628
4	⅜	0·711	0·598	0·710
5	⅜	0·763	0·665	0·762

As appears in this Table, a series of narrow divisions arise from this part of the integral.

On applying the ratios to the satellite Mimas, we have the following series of divisions. They are worked to two places of decimals, in order to show the order of magnitude of the width of the divisions.

For $n = 2$, 12·90″ to 12·81″,

$n = 3$, 16·89″ to 16·85″,

$n = 4$, 19·08″ to 19·03″,

$n = 5$, 20·50″ to 20·45″.

The first division is in the Crêpe Ring, just within the commencement of Ring B, the inner diameter of which is 13·00″.

The second division is at the inner edge of Cassini's Division.

The third division is a new one and falls almost exactly in the position given for Encke's Division. Lowell[*] gives the radius of Encke's Division as 19·00″; while See[†] states it at 18·87″ with a width of 0·41″. In either case theory clearly indicates the existence of this division.

The third division again falls outside the existing ring.

Applying next the ratios in the Table to the satellite Enceladus, the only case to be mentioned is the value when $n = 2$. This should give a division extending from 16·56″ to 16·44″.

[*] 'Lowell Observatory Bulletin,' No. 68.

[†] 'Astr. Nach.,' No. 3766.

There is no observed division at this position that I have been able to find. But it is easy to show that it must be very indefinite. The value of the inclination of the orbit of Enceladus is 1·3′ compared with 36′ for that of Mimas. The effect of the inclination must, therefore, be less marked in the former case. Again, if we compare the distance of the satellite producing the Encke Division from that division with that of Enceladus from the new division, taking ratios (as that is the form in which the distances appear in the analysis) we find $a/a' = 0·7$ for Encke's Division and $a/a' = 0·48$ for the new division. The perturbing effect of Mimas in Encke's Division is, therefore, much greater than that of Enceladus in the new division. On these two counts we should expect the new division to be less distinct than Encke's Division. But Encke's Division is only visible with difficulty; hence it is to be expected that the new division should be unobservable.

None of the remaining satellites produce divisions corresponding to the formulæ of this paper within the existing Ring system.

§ 5. *Summary.*

The effect of a satellite moving in an orbit inclined to the plane of the Rings of Saturn is to produce one new division. If the satellite be taken as Mimas, a narrow division will be caused at a distance 19·05″ from Saturn. This closely corresponds with the observations of Encke's Division.

Enceladus should produce a division at 16·5″. No observed division is recorded at this place, but because of the minute inclination of the orbit of Enceladus and because of this satellite's distance from this place, it is to be expected that the division will be comparatively feeble.

On the Analysis by Positive Rays of the Heavier Constituents of the Atmosphere; of the Gases in a Vessel in which Radium Chloride had been stored for 13 Years, and of the Gases given off by Deflagrated Metals.

By Sir J. J. Thomson, O.M., F.R.S.

Sir James Dewar was kind enough to supply me with large quantities of the residues obtained from the evaporation of many thousand tons of liquid air. These residues had been absorbed by charcoal which had been kept in a sealed vessel. I have analysed these residues by the Positive Ray Method. The general arrangements were the same as those described in my book on Positive Rays. Some alterations, however, were necessary, as I used for these investigations a much more powerful induction coil than the one I had hitherto employed. With this coil so much heat was developed in the part of the tube near the cathode that any wax joints in that neighbourhood, even though they were cooled by a water jacket, gave off enough gas to spoil the vacuum for positive ray purposes. To avoid this difficulty I substituted for the wax joint, which formed the connection between the glass bulb in which the discharge takes place and the brass vessel which contains the camera, a joint made by a method used by Mr. Roebuck, and described by him in the 'Physical Review,' vol. 28, p. 264 (1909). The method consists in first making on the outside of the glass tube a deposit of platinum by one or other of the devices used for platinising glass, and then depositing slowly by electrolysis a layer of copper on the platinum. With care this layer can be made thick and firm enough to enable a brass tube connected with the camera vessel to be soldered on to it, and an air-tight joint obtained which does not give off gas when heated by the discharge.

The method adopted to analyse the gas was to put some of the charcoal containing the gaseous residues into a small vessel A, which was fused on to the discharge tube B; there was a tap between A and B, and this was turned until B had been exhausted to a very low pressure; there was also a very fine capillary tube in the circuit between A and B, and when the pump used for exhausting the discharge tube was kept in action a continuous stream of gas from A could be kept flowing through the discharge tube without making the pressure too high to obtain good photographs. Just

before the tap between A and B was opened a photograph was taken with ordinary air going through the discharge tube, and the lines in this were compared with those on the photograph obtained when the gas from A was flowing through the tube.

As the charcoal was found to have absorbed large quantities of water vapour, it was necessary to have a phosphorus pentoxide in connection with A for several days before a photograph was taken, otherwise so much water vapour came out of the charcoal that the pressure in the discharge tube got so high that sharp photographs could not be taken. The charcoal also contained a considerable amount of mercury vapour. The bulb A was placed in a bath and photographs were taken with A at the temperature of the room, at 100° C., and at the highest temperature the bulb would stand without softening. The difference in the photographs at different temperatures consisted in variations in the intensity of the lines rather than in the absence or presence of new lines. The most striking characteristic of the photographs obtained with the residual gas was the predominance of the xenon line over all the lines due to the other inert gases. The xenon line was very strong, but in the first few photographs I could not detect either the krypton or the neon lines. As, however, the inert gases get absorbed by the electrodes to a very remarkable extent, they tend to accumulate in the electrode after the discharge has been maintained for a long time, and after about 20 photographs had been taken I could just detect the krypton line ; it never, however, was otherwise than exceedingly faint, and the quantity of krypton in the residual gas must be very small indeed compared with that of the xenon. I was never able to detect the neon line. The evaporation of the gases from the charcoal seems to have effected a fractionation, with the result that there is a great excess of the heavier gas in the fraction retained by the charcoal.

In addition to the xenon line there were two faint lines of great interest, both indicating gases of greater atomic weight than xenon. The stronger of the two lines has a value of m/e equal to 163 ± 5, the weaker has $m/e = 260 \pm 10$. The lines are so faint that it is difficult to get very accurate measurements. A great deal, however, can be done in the measurement of faint lines by a proper choice of the intensity of the illumination. These lines are very difficult to see in a strong light, but when the intensity of the illumination is reduced they may become quite distinct and measurable. It is convenient to measure these lines in a room where the illumination varies considerably from place to place, and to move about until the most favourable place for good seeing is found.

Origin of the Lines 163 and 260.

These lines might, as far as their atomic weights go, originate from molecules of krypton and xenon respectively, and I am inclined to think that this is the correct interpretation, there are, however, many properties of these lines which seem at first sight to be incompatible with this explanation. For example the line 163 frequently occurs on photographs when the line due to krypton itself cannot be detected, again I have positive ray photographs, taken when the gas in the discharge tube was rich in krypton, where the krypton line is very strong, but which do not show any trace of the line 163. This objection would be fatal were it not for the way in which the residual gases we are considering had been collected and stored. Let us assume for a moment that molecules of krypton can exist, but that when krypton is in the gaseous state the molecules are few compared with the atoms ; let us now suppose that this mixture is absorbed by cold charcoal and then allowed to evaporate slowly. Since the Kr molecules are more complex than the atoms they will probably be much more firmly held by the charcoal so that the atoms will evaporate much more rapidly than the molecules, thus the residue in the charcoal will get richer and richer in molecules as compared with atoms. In fact we may suppose that the explanation which we gave to explain why the residual gas was much richer in Xe than in Kr, though there is more krypton than xenon in the atmosphere, can be extended to explain why, though the Kr molecules in the atmosphere are few compared with the atoms, they are in the majority in the residues.

As molecular krypton would be heavier than atomic xenon it would probably not come out of cooled charcoal any more readily, if so readily as xenon. Thus the ordinary method of separating krypton from xenon would separate the atomic but not the molecular form of this gas. Thus xenon obtained in this way would contain some krypton which, when a spark was passed through the mixture, might give rise to the krypton spectrum. Professor Moore has prepared xenon which does not show the krypton spectrum. It must be remembered, however, that the positive ray photographs indicate that the quantity of the substance giving the line 163 in the atmosphere is an exceedingly small fraction of the amount of xenon, and in some mixtures of two gases the spectrum of one of the constituents is not excited unless more than a certain percentage of it is present in the mixture.

There is one important respect in which the substance giving the line 163 shows the characteristics of an atom rather than those of a molecule, for

on two or three of the strongest photographs it can be seen that this line is prolonged towards the axis, which indicates that the source of this line can carry a double charge of electricity. A double charge of electricity is in the great majority of cases confined to atoms, though there are a few instances known where the molecule of a compound carries a double charge.

The strongest argument in support of the view that this line is due to a molecule of krypton, and not a new element, is that such an element would not fit in well with the periodic law. It is perhaps possible to lay too much stress on this argument, for the atomic weight would indicate that the element would be in the parts of the table covered by the rare earths, a region where there seems to be great confusion.

The existence of molecules of inert gases is of considerable interest. I have shown from the evidence given by positive ray photographs that charged molecules of helium occur in the discharge tube. We do not know, however, whether such molecules could exist without a charge. If the line 163 is due to a molecule of krypton, this molecule must be stable when uncharged. The existence of molecular krypton would indicate that this element, like some others, could show two valencies, the normal zero valency and another. If this is so we might expect krypton to combine with some of the other elements to form compounds. Such a compound may be the origin of another line, which I have observed in the positive ray spectrum of the gas supplied to me by Sir James Dewar; this line corresponds to an atomic weight of about 118; it is not like the lines 160 and 260 found on all the plates, but only on a few of them; when it does occur, however, it is stronger than either of these lines. I have never been able to get the line 260 sufficiently intense to feel sure that I could see a prolongation if there was one.

From these experiments we conclude that the atmosphere contains small quantities of two constituents heavier than xenon. As the molecular weights of these are about twice the atomic weights of krypton and xenon it seems probable that these heavier constituents are molecules of krypton and xenon. The lighter of the two constituents is more abundant than the heavier, but the amount of either is only a very small fraction of that of xenon.

I made experiments to see if these constituents showed any properties analogous to those of the emanations of radio-active substances. If such emanations are placed in a closed vessel they increase the ionization in the vessel and consequently the rate of leak of a charged insulated body placed inside the vessel. I could not, however, detect any change of leak when the gases which had been absorbed by the charcoal were introduced into an ionization vessel.

Gases Obtained from a Tube which had Contained Radium for Thirteen Years.

The Royal Society were kind enough to allow me to have the use of the 70 mgrm. of RaCl$_2$ which had been used by Sir T. E. Thorpe in his determination of the atomic weight of radium, and by Sir James Dewar in his experiments on the amount of helium given off by radium. The radium had been sealed up in a glass tube from which the air had been exhausted by Sir James Dewar in 1909.

To analyse the gases in this tube I found it necessary to construct a new positive ray apparatus, as the one that had been used for the preceding experiments had got so contaminated with xenon that I was unable, either by repeated sparking or by passing continuous currents of air through the tube, to get rid of indications of the xenon line on the photographs.

The operation of transferring the gases from inside the sealed radium tube to the discharge tube without introducing other gases presented considerable difficulty; a very satisfactory solution was obtained by using the following method.

The radium tube was placed in a vessel A, which was connected with the discharge tube B by a circuit containing a tap and fine capillary tubes for regulating the rate of flow from the gas in A through B. A side tube was
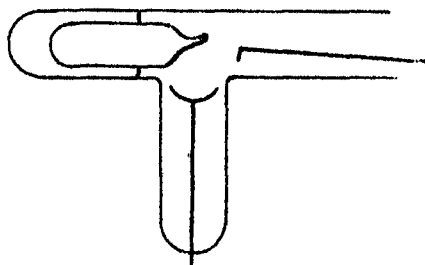
attached to A and in this there was a concave electrode which, when it was used as a cathode, caused a beam of cathode rays to focus on the tube containing the radium, the impact of these rays bored a small hole through the radium tube through which the gases from this tube could pass into the discharge tube. The adjustment for the right position of the radium tube and the concave cathode was made by taking a dummy tube of the same size and shape, and as nearly as could be judged of the same thickness as the radium tube. When this had been adjusted so that a hole was invariably pierced through the tube when the cathode rays were turned on, the dummy was replaced by the radium tube, and this was successfully pierced by the cathode rays. I had expected that owing to the long exposure to the radium the glass would be likely to explode when it was fractured, and precautions were taken

to prevent any loss of radium or fracture of the tube A should this happen. Nothing of the kind however occurred, and there was not even a trace of a crack round the hole.

It should be mentioned that before the cathode rays were turned on, the discharge tube and the vessel A were exhausted to a high vacuum by a Gaede pump and cooled charcoal. A photograph was taken just before the radium tube was pierced and another immediately after. On examining the photograph taken after the gas from the radium had got into the discharge tube it was found, as might be expected, that it showed a very strong helium line ; the only other line which was not on the plate taken just before the radium tube was pierced was a very faint line for which $m/e = 5$. I could not see either the neon line or that corresponding to H_3. The lines due to the atom and molecule of hydrogen were very strong on both photographs. It must be remembered that the tube in which the radium was contained had been exhausted before sealing so that the α-particles from the radium had nothing to bombard except the walls of the tube and the radium chloride itself.

I have opened at one time or another several tubes which have contained radium for considerable periods though none for so long as the one now under consideration. These showed the " 3 " line and some of them the neon line. It must be remembered, however, that these tubes had not, like the present one, been highly exhausted, but were full of air at atmospheric pressure. I did not observe the " 5 " line on the older photographs, but these were not nearly so sharp and distinct as those taken with the present tube.

As the " 5 " line appears on photographs which do not show any trace of lines corresponding to $m/e = 10$ or 20, it is not likely to be due to a doubly charged atom ; a molecule containing one atom of helium and one of hydrogen would give a line for which $m/e = 5$, and considering that in the radium tube there is both helium and hydrogen, and that these have been exposed to the action of α-rays, it is, I think, probable that the line is due to this compound.

After all the gas which had come out of the radium tube had been utilised for taking photographs, the bulb A was filled with air which was left for several days standing over the radium, then some of this gas was put into the discharge tube and positive ray photographs taken. One of the features of these photographs was the intensity of the lines corresponding to the doubly charged atoms of oxygen, nitrogen, and carbon. These lines are always found in good photographs of air, even though it has not stood over radium ; but the radium seems to produce a considerable increase in their intensity. It is not, however, the only agent that does so, for I have found that the gases given off when very fine metallic wires are deflagrated by powerful electric currents also give rise to photographs in which the lines due to these doubly

charged atoms are very much enhanced in intensity. I have succeeded in obtaining photographs on which these lines are as strong as any on the plate.

The study of these enhanced lines has brought out many interesting features which were not detected with the fainter lines of the earlier photographs. One of the most important of these is that the lines due to the doubly charged atoms, like those due to the simply charged ones, show prolongations towards the vertical axis. If d is the normal minimum distance from the vertical axis, *i.e.*, d is the minimum electrostatic displacement of a singly charged atom, then it was found that on many of the plates the lines due to the doubly charged atoms of oxygen, nitrogen, and carbon were prolonged, so that the minimum electrostatic displacement was only $2d/3$. On a few of the best plates the lines corresponding to the doubly charged oxygen and nitrogen atoms were prolonged until the minimum electrostatic displacement was only $d/2$. I could not be sure that the prolongation of the line due to the carbon atom was as great as this. The prolongation beyond the normal stopping-place indicates* that some of the carriers had while in the discharge tube a greater charge, and so by falling through the same potential difference acquired greater energy than the normally charged atom. They lost the extra charge after leaving the discharge tube and before being photographed, so that the value of m/e for the prolongation is the same as for the main portion of the curve.

The energy possessed by a carrier is inversely proportional to its displacement by the electrostatic field, and since the energy is proportional to the charge carried by the particle in the discharge tube, this charge will be inversely proportional to the minimum distance of the parabola from the vertical.

Thus, if a parabola has a prolongation such that the minimum distance of a point from the vertical is $d/2$, while d is the normal minimum distance, it shows that the carrier which gives rise to the parabola can occur in the discharge tube with twice the normal charge. If the prolongation only extends to $2d/3$ it shows that the carrier can occur in the discharge tube with a charge $3/2$ times the normal charge. By the normal charge we mean the charge carried by the particles while they are passing through the electric and magnetic fields. Now in the lines corresponding to the doubly charged atoms of oxygen, nitrogen and carbon, the normal charge is two units, hence, since these show a prolongation extending to $2/3$, some of these atoms must have had in the discharge tube a charge equal to $(3/2) \times 2$ or 3 units. While since the lines due to oxygen and nitrogen show a prolongation to $d/2$, some of these atoms must have had in the discharge

* See 'Rays of Positive Electricity,' 2nd edition, p. 77.

tube a charge equal to 2×2, *i.e.*, 4 units.   If some of the atoms retained their triple charge while passing through the electric and magnetic fields we should have parabolas for which m/e was for oxygen, nitrogen, and carbon 16/3, 14/3, 12/3 respectively.   I have plates on which the first two of these are quite visible.   If the atoms retained their quadruple charges there would be parabolas for which $m/e = 16/4$, 14/4 for the oxygen and nitrogen atom respectively; these parabolas are, however, so faint that I have not been able to detect them.   The amount of prolongation of the parabolas corresponding to the doubly charged atoms shows, however, that atoms with four-fold charges must exist.

This result has an important bearing on the question of the number of electrons in the outer layers of the atoms of carbon, nitrogen and oxygen. For since each unit of positive charge involves the removal of an electron from the outer layer of the atom, and since atoms of oxygen and nitrogen with four charges and atoms of carbon with three have been detected by the positive rays, the atoms of oxygen and nitrogen cannot have less than four electrons in the outer layer, nor can the atom of carbon have less than three.   These results are thus in accordance with the view that the atom of oxygen has six, the atom of nitrogen five, and the atom of carbon four electrons in the outer layer.

A very interesting line, for which $m/e = 10$, was first detected on some plates on which the lines due to the doubly charged atoms were exceptionally well developed.   When attention had once been called to its existence, closer scrutiny of the earlier plates showed that a faint line in this position is by no means uncommon.   When neon is in the tube a line corresponding to $m/e = 10$ is generally found, but this is always accompanied by a much stronger one for which $m/e = 20$.

The peculiarity of the line we are now considering is that it occurs when there is no trace of a line for which $m/e = 20$, and when there is no reason for suspecting the presence of neon.   If the line is due to a singly charged atom it involves the existence of a new element; on the other hand, if it is due to a doubly charged one we have to explain the absence of the line due to the singly charged atom.   An explanation which surmounts these difficulties is that the line is due to a doubly charged oxygen atom combined with four atoms of hydrogen.   A doubly charged oxygen atom has lost two electrons and thus has four left in the outer layer, the same number as are in an uncharged atom of carbon.   The valency of the doubly charged oxygen atom will thus be the same as that of carbon, so that it can form the compound $O\_ \_ H_4$; the value of m/e for this is 10.   As the existence of this compound depends on the double charge on the oxygen atom it could

not exist with a single charge, hence the absence of the line $m/e = 20$. The singly charged oxygen atom would have five electrons in the outer layer and would therefore have the same valency as the neutral nitrogen atom, it could form the compound O_H_3. The value of m/e for this is 19, and a line with this value of m/e is one of the lines which occur most frequently on photographs of the positive rays.

Gases given off when Metallic Wires are Deflagrated.

It has recently been asserted that helium is given off in considerable quantities when thin metallic wires are deflagrated by powerful electric currents. Some time ago I found that small quantities of helium were given out by many substances when bombarded by cathode rays; the quantity was very small and the emission ceased after the bombardment had lasted for some time. I could not detect any helium if the substance were merely heated without bombardment by cathode rays. I have recently tested by the Positive Ray Method the gases given off when fine wires of tungsten, gold, or copper are deflagrated by powerful electric currents. I could not detect any helium, the H_3 line was however quite strong. This is in agreement with my earlier experiments when I found I could get H_3 but not He by heating without bombardment.

Summary.

The paper contains an account of applications of the Positive Ray Method of Analysis to several problems. The first is that of the heavier constituents of the atmosphere. It is shown that at least two constituents heavier than xenon are present in the atmosphere. The approximate values of the atomic weights are 163 and 260; the lighter of these is the more abundant, but the quantity of it in the air is very small compared with that of xenon.

The source of these lines is discussed; on the whole, it seems most probable that they are due to molecules of krypton and xenon.

These gases were observed in the residues of large quantities of liquid air which were very kindly placed at my disposal by Sir James Dewar.

The second application was to the analysis of the gases in the sealed tube in which the radium chloride belonging to the Royal Society had been sealed for thirteen years; the tube had been exhausted by Sir James Dewar before sealing. In the photographs obtained with this gas the helium line was very strong; there was no neon, there was however a faint line for which $m/e = 5$, due probably to a compound of helium and hydrogen.

The analysis was also applied to gases which had stood over radium and also to the gases lit by deflagrating wires. From the study of the photographs obtained with these gases, quadruply charged atoms of oxygen and nitrogen

were detected and triply charged atoms of oxygen, nitrogen, and carbon. The compound OH_4 was also detected carrying invariably a double charge.

I am much indebted to the Royal Society for the loan of the radium; to Sir James Dewar for placing at my disposal large supplies of the residues of liquid air, and to Mr. E. Everett for the assistance he has given me in making the experiments.

On the Scattering of β-particles.

By B. F. J. SCHONLAND, O.B.E., M.A., George Green Student of Gonville and Caius College, Cambridge.

§ 1. *Introduction.*

An account has recently been published* by Dr. J. A. Crowther and the writer, of some experiments on the scattering of β-rays by thin sheets of matter. The angles of deflection investigated ranged from 4° to 8°. The main results obtained may be summarised as follows :—

(1) The scattering observed was " single," *i.e.*, due to one collision with an atomic nucleus.

(2) The law of force governing such collisions appeared to be that of the inverse square.

(3) The single scattering theory due to Sir Ernest Rutherford requires the scattering power of an element to be proportional to the square of its nuclear charge. This relation was found to hold only in the case of the elements carbon and aluminium, if the nuclear charge consist of as many positive units as the atomic number of the element.

(4) For the elements copper, silver, gold and platinum, a comparison with previous results extending the range of the deflection angle to 20°† showed that a rapid increase in the scattering power of these elements appeared to take place as the thickness and angle of deflection were increased.

The experiments to be described were instituted to test the truth of (4) and to confirm the other conclusions under the somewhat easier experimental conditions prevailing at larger angles of deflection. They were carried out at from 12° to 25°.

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* Crowther and Schonland, ' Roy. Soc. Proc.,' A, vol. 100 (1922).
† Crowther, ' Roy. Soc. Proc.,' A, vol. 84 (1910).

A further conclusion reached in the previous paper was that the numerical value of the scattering observed was 2·9 times greater than that to be expected on the theory mentioned. This conclusion, which does not affect those given above, was also examined and found to be incorrect.

In a recent paper Geiger[*] has given results of an investigation of this problem by the photographic method, which confirm (2), (3) and (4).

§ 2. *Experimental Arrangement.*

The apparatus used was similar to that described in the previous paper, modified however to deal with angles of deflection from 12° to 25°. The angular divergence of the β-ray beam was proportionately increased, giving an ionisation effect which was some ten times greater than before.

This made easy an examination of the sources of error in the arrangement, directed towards the following points:—

(1) A possible effect of the stray magnetic field on the scattered particles. This was found to be negligible, the magnetic shielding being ample.

(2) A possible difference between the velocity of the β-rays examined and that calculated from the bending in the magnetic field. A proportion of the beam might consist of scattered and secondary β-particles from the walls of the bending chamber and firing tube. Such rays of sufficient penetrating power to pass into the measuring chamber were found not to constitute as much as 1 per cent. of the beam.

(3) An effect due to the divergence of the beam. This was found to be very important.

§ 3. *The Error in Absolute Value due to Divergence of the Beam.*

The usual arrangement of the experiments is shown in diagrammatic form in fig. 1.

The shaded area represents the beam of rays, PQ the circular aperture, and AB the scattering foil. Rays incident on the foil in the direction OA will, after scattering, be faced with an angular aperture which is not ϕ, but varies from θ_1 to θ_2 with their scattered direction. If we suppose the beam to be annular in cross-section, *i.e.*, concentrated at the edges of the cone OA, OB, integration shows that the observed scattering will be greater than that calculated, by the factor

$$\gamma = \frac{\sec^3 \phi}{(1 - \alpha^2/\phi^2)^2}, \text{ where } \alpha = \tfrac{1}{2} \text{ angle of divergence of beam,}$$
$$\phi = \tfrac{1}{2} \text{ angular aperture,}$$
$$= 1·7 \text{ for } \alpha/\phi = 0·4 \text{ and } \phi = 20°.$$

[*] Geiger, ' Zeitschrift für Physik,' vol. 6 (1921).

If, however, the beam is supposed uniform over its cross-section, the value of γ is only 1·1.

The experimental examination of the value of γ was effected by reducing the divergence of the beam in steps until it had the form shown in fig. 2.

FIG. 1.
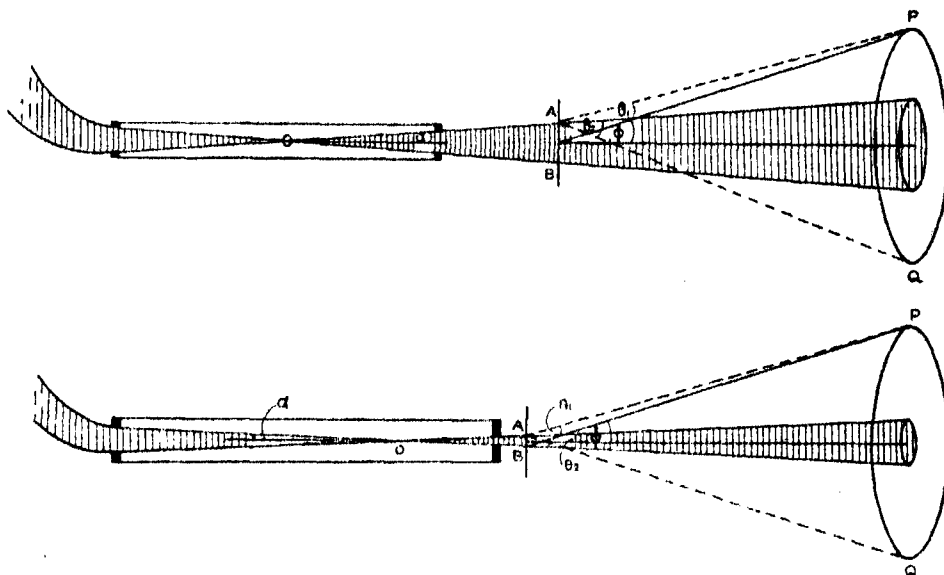
FIG. 2.

The effect produced on the observed scattering is shown in fig. 3. Curve I corresponds to fig. 1, curve III to fig. 2, and curve II to an intermediate arrangement. It is seen that the scattering (I/I_0) is decreased 1·8 times by
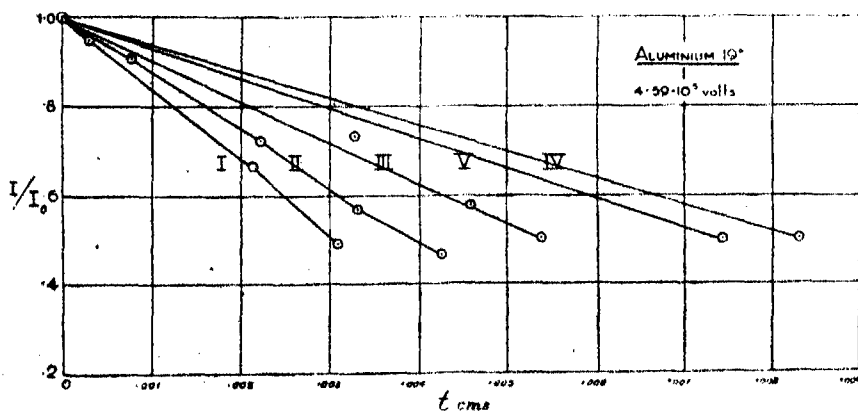
FIG. 3.

changing the conditions from fig. 1 to fig. 2. Curve IV is the calculated scattering curve, and curve V is obtained from this by an alteration of 10 per cent. This is warranted by the consideration that the effects of absorption and reflection of rays by the aluminium window closing the scattering chamber vary as $\sec^2\phi$, and ϕ is here about 20^c.

The final curves, III and V, differ by 28 per cent. in the value of I/I_0 for a given thickness. A precisely similar set of curves was obtained for $\phi = 25°$, the difference here being 26 per cent. In view of small residual errors due to the divergence of the beam and other causes, the agreement between theory and experiment is as near as could be expected from the experimental arrangement. The results give a value for the nuclear charge of aluminium of about 15 units, instead of the atomic number 13.

Photographs of the beam were taken to investigate the distribution of the rays over the cross-section. They show a decided tendency towards an annular distribution, which, as has been seen, would explain the effect observed.

§ 4. *The Variation of Scattering with Angle of Deflection.*

On the single nuclear scattering theory applied to β-particles, the fraction scattered through an angle greater than ϕ

$$\rho = \frac{\pi}{4} \, nt \, b^2 \cot^2 \frac{\phi}{2} f^2(\phi, \beta). \qquad (1)$$

Here $n =$ no. of atoms p. u. vol., and is const. for Au, Ag, and Al,

$$b = \frac{Ne^2}{[\text{Energy}]}, \text{ the energy being expressed by the Planck-Einstein formula,}$$

$f^2(\phi, \beta)$ is the relativity correction (*vide* Sec. 6).

At constant energy (1) reduces to

$$\rho = \text{const.} \times \frac{tN^2}{\phi^2}, \text{ since } f^2(\phi, \beta) \text{ varies slowly with angle } \phi,$$

or if $t = t_m$ when $\rho = \frac{1}{2}$,

$$\frac{\phi^2}{t_m} :: N^2. \qquad (2)$$

Thus the curve for each element relating ϕ and t_m should be a parabola with latus rectum proportional to the square of its atomic number. Fig. 4 shows that for aluminium this parabolic relation is followed throughout the range examined. For heavier elements the parabola becomes a straight line as the thickness t_m diminishes.

Curves similar to those above have been recently found by Geiger,[*]

* Geiger, *loc. cit.*

using the photographic method. Taking the parabolic portions of the curves the Table below shows that relation (2) is approximately fulfilled.
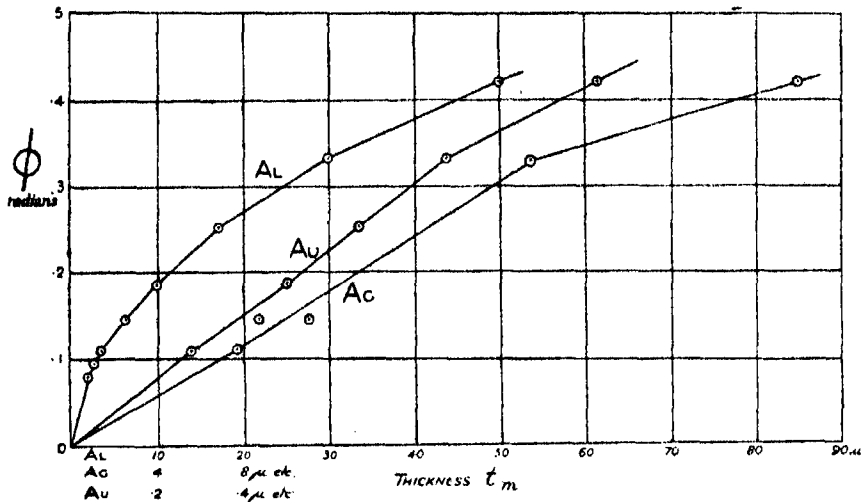
FIG. 4.

Element.	t_m for $\phi = 0\cdot42$ radians.	$t_m \times N^2$.
	cm.	
Al	0 ·0050	84
Ag	0 ·00034	75
Au	0 ·000124	78

The behaviour of aluminium is shown by the constancy of $\phi/\sqrt{(t_m)}$ in the Table below.

ϕ.	$\phi/\sqrt{(t_m)}$.	
5	5 ·90	
6	5 ·95	Published in previous paper.
8	5 ·92	
10 ·5	5 ·98	
14 ·3	6 ·04	
18 ·9	6 ·04	
24 ·0	5 ·88	

For gold and silver, after a certain critical value for t_m, ϕ/t_m is found to be approximately constant, as fig. 4 shows. An explanation of this apparent anomaly follows.

§ 5. *The Screening Effect of Electrons in the K and L Rings.*

The results given show that as the thickness is reduced, the scattering of β-rays by the elements Au, Ag and Cu falls *below* the theoretical value as soon as a certain critical thickness is passed. This thickness has not been reached for aluminium or carbon.

The falling off in the scattering power is progressive and continuous. For gold the reduction has been pushed to one-third of the original scattering power.

The phenomenon would be explicable if there were reason to suppose that as the thickness t_m of the foil is diminished by reducing the observed angle of deflection ϕ, the effective nuclear charge responsible for scattering is in some way diminished too. Such an explanation is offered by the screening action of the electrons surrounding the nucleus in the K and L rings.

If t_m is the thickness, d_m the distance within which one-half of the incident particles come to some one nucleus, n the number of atoms per unit volume,

$$\pi n t_m d_m^2 = \tfrac{1}{2},$$

or

$$d_m :: \frac{1}{\sqrt{(t_m)}}.$$

Thus as the thickness is diminished the distance of approach which corresponds to t_m increases. Provided it can be shown that this increase of d_m brings the orbit of the β-particle into the region occupied by the electrons, the decrease of the effective nuclear charge receives an explanation. In spite of the fact that in these experiments we are dealing with particles whose distances of approach to the various nuclei that deflect them are not all equal, the distance d_m and the information about the nuclear charge derived from it are perfectly definite. For d_m is that distance of approach to a nucleus for which the particle is *just* deflected through an angle ϕ.

The experiments show that at all the values of d_m examined the nuclear charge for aluminium is constant and equal to its atomic number within the error of experiment. For gold, the nuclear charge varies from 79 to 51 units as d_m is increased. For silver similar results hold, but the constant and correct value of the nuclear charge is reached before d_m has the lowest value examined.

If, as has been suggested, the electrons in the "rings" surrounding the nucleus produce this reduction in the effective nuclear charge, it must be shown that the distances d_m for the various elements are such as to bring the orbits of the β-particles under the influence of these electrons to the extent

required. This means that in all the experiments with aluminium the β-particles penetrate inside the K ring of that element, while in the case of gold these orbits are described with the electrons of the K ring, and other outside electrons, intervening between the β-particles and the nucleus. The Table below shows that this is the case. The maximum and minimum values of d_m given correspond to angles of deflection of 6° and 25°. They should be compared with the calculated values of the "radii" of the rings. The last two columns give the maximum reduction in the atomic nuclear charge n_{obs} (this is found at d_m max.), and a calculated value of n which will be discussed.

Fig. 5 gives a representation of the tabulated results, drawn to scale.

Element.	d_m (min.).	d_m (max.).	r_L.	r_K.	n_{obs}.	n_{calc}.
	cm.	cm.	cm.	cm.		
Al............	$2\cdot3\,.\,10^{-11}$	$9\cdot0\,.\,10^{-11}$	—	$5\cdot4\,.\,10^{-10}$	0	0
Ag............	$9\cdot0\,.\,10^{-11}$	$2\cdot0\,.\,10^{-10}$	$5\cdot0\,.\,10^{-10}$	$1\cdot0\,.\,10^{-10}$	16	3 to 16
Au............	$1\cdot5\,.\,10^{-10}$	$3\cdot0\,.\,10^{-10}$	$3\cdot4\,.\,10^{-10}$	$7\cdot0\,.\,10^{-11}$	26	16
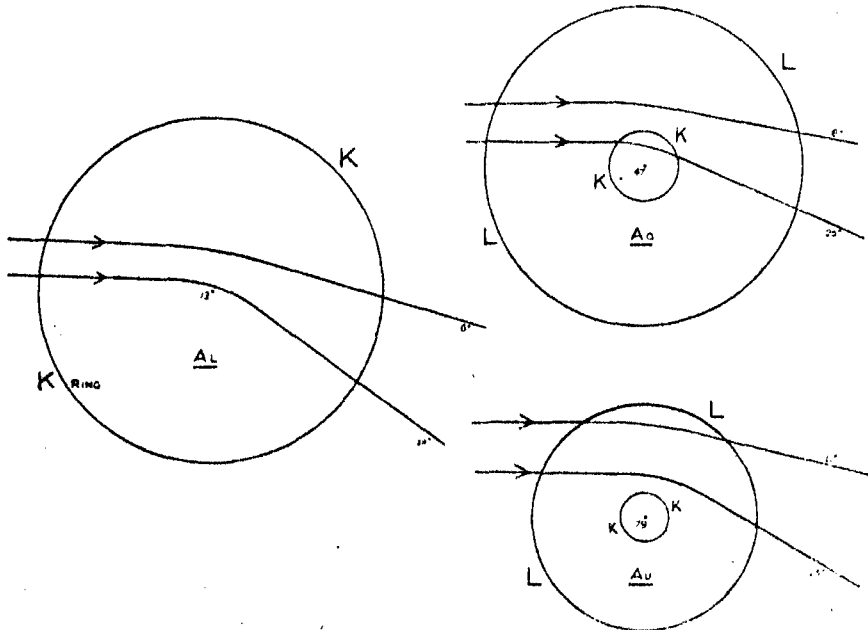
Fig. 5.—1 cm. $= 10^{-10}$ cms.

The calculations of r_L and r_K as well as n_{calc} have been made as follows. The Bohr theory of the hydrogen atom can be applied to this purpose in the case of more complex atoms only indirectly. This is due to the effect

mentioned, namely the screening of the nucleus by successive rings, and to the mutual repulsion of the electrons themselves. Any deduction of the radii based entirely upon theory has less weight than the results to be obtained from X-ray absorption spectra. The method used for getting the figures tabulated above is :—

(a) Calculate N_{eff}, the effective nuclear charge at the K or L ring from the equation

$$N_{eff}^2 \cdot \nu_H = \nu_E \text{ where } \nu_H \text{ is the frequency of the } \begin{cases} \text{first} & \text{Bohr ring for} \\ \text{second} & \text{Hydrogen,} \end{cases}$$

and ν_E is the maximum absorption frequency of the $\begin{cases} \text{K} & \text{X-ray spectrum of the} \\ \text{L} & \text{element considered.} \end{cases}$

Then $n_{calc} = N - N_{eff}$.

The following approximate values for n_{calc} hold for elements between Al and Au.

	K ring.	L ring.	M ring.
n_{calc}.	3	16	30

(b) Consider the electrons as revolving in simple Bohr orbits round the nuclear charge N_{eff}.

Then
$$r_K = \frac{0.538 \cdot 10^{-8}}{N_{K\,eff}} \text{ cms.,}$$

$$r_L = \frac{4 \times 0.538 \cdot 10^{-8}}{N_{L\,eff}} \text{ cms.,}$$

$N_{K\,eff}$ and $N_{L\,eff}$ being the values of N_{eff} at the K and L rings.

The assignment of definite values to these "radii" is, of course, to some extent artificial, for on Bohr's later views the electrons have complicated orbits round the nucleus. Their distribution will thus resemble a diffuse cloud more than a discontinuous set of rings. The calculation of n given is more likely to be correct than any deduction at present possible which is based on the theoretical distribution and orbits of the electrons. That n_{calc} is likely to be less than n_{obs} is clear from the fact that only at its *nearest* point of approach to the nucleus does the β-particle come under as large an effective nuclear charge as $N - n_{calc}$. Thus the higher values of n_{obs} are to be expected.

It is interesting to compare these results with some early experiments of Geiger[*] on the scattering of α-particles by thin foils of gold, where the same effect is shown. The table gives his experimental figures, the most probable angle of deflection (which is $\phi/1.18$) being termed λ. p is the correction to

* Geiger, 'Roy. Soc. Proc.,' A, vol. 81, p. 174 (1908).

λ for loss of velocity in passing through the foil, and in the final column is $\lambda p/\sqrt{(t)}$ which should be constant. For small thicknesses this is not true and the critical thickness is found to be about the same as in the present experiments, namely, that at which the most probable distance of approach reaches the neighbourhood of the L ring.

No. of foils t.	Stopping power.	λ.	p.	$\lambda p/\sqrt{(t)} \times 10.$
	cm. (air).	′		
1	0·04	10	1·0	1·00 ⎫
2	0·08	23	1·0	1·62 ⎬ Outside region of L ring.
4	0·15	36	1·0	1·80 ⎭
8	0·29	49	0·985	1·78
12	0·46	70	0·98	1·96
20	0·76	100	0·97	2·14
30	1·14	140	0·94	2·40

§ 6. *The Orbit of a β-particle in Collision with a Positive Nucleus.*

The following deduction of a "relativity correction" to the original Rutherford theory of scattering of α- and β-particles is based on a paper[*] on β-ray absorption by Mr. C. G. Darwin and a further application of it to the present problem which he very kindly worked out for me.
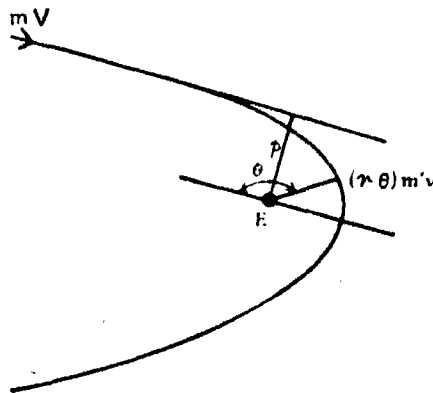
Fɪɢ. 6.

Let V = initial velocity of the particle,

m = initial mass,

v = velocity at pt r, θ,

m' = mass at pt r, θ.

Then $\qquad m' = \dfrac{m_0}{(1-v^2/c^2)^{\frac{1}{2}}}$ and $\quad m = \dfrac{m_0}{(1-V^2/c^2)^{\frac{1}{2}}}.$

[*] C. G. Darwin, 'Phil. Mag.,' vol. 25, p. 201 (1913).

From the conservation of angular momentum

$$m'r^2\dot\theta = mp\mathrm{V},$$

where p is the perpendicular from the nucleus of charge E on the original direction of motion,

or
$$\frac{r^2\dot\theta}{(1-v^2/c^2)^{\frac{1}{2}}} = \frac{p\mathrm{V}}{(1-\mathrm{V}^2/c^2)^{\frac{1}{2}}}. \tag{3}$$

From the conservation of energy

$$m_0c^2\left\{\frac{1}{\sqrt{(1-v^2/c^2)}}-1\right\} = m_0c^2\left\{\frac{1}{\sqrt{(1-\mathrm{V}^2/c^2)}}-1\right\}+\frac{\mathrm{E}e}{r},$$

or
$$\frac{1}{\sqrt{(1-v^2/c^2)}} = \frac{1}{\sqrt{(1-\mathrm{V}^2/c^2)}}+\frac{\mathrm{E}e}{m_0c^2}\cdot\frac{1}{r}. \tag{4}$$

From (3) and (4), eliminating v

$$r^2\dot\theta = \frac{pc\sin\beta}{1+(a/r)\cos\beta}, \qquad \left[\begin{array}{l}\sin\beta = \mathrm{V}/c\\ a = \mathrm{E}e/m_0c^2.\end{array}\right.$$

From (4)
$$\dot r^2+r^2\dot\theta^2 = c^2\left\{1-\frac{\cos^2\beta}{(1+(a/r)\cos\beta)^2}\right\}.$$

By integration from these last two equations, the orbit is

$$\frac{p\gamma}{r} = \sin\gamma\theta+(1-\cos\gamma\theta)\frac{cp_0}{\mathrm{V}\gamma p},^*$$

where
$$p_0 = a\cot\beta,$$
$$\gamma^2 = 1-p_0^2/p^2.$$

This orbit is described in the paper quoted. In the cases to which it is here applied we do not need to consider the spiral form it may assume. Nor does loss of energy by radiation play any part in these collisions.

Writing $p = p_0\operatorname{cosec}\psi$ we find $\gamma = \cos\psi$ and the orbit is

$$\frac{p\gamma}{r} = \sin(\theta\cos\psi)+[1-\cos(\theta\cos\psi)]\frac{c}{\mathrm{V}}\tan\psi.$$

If the deflection is ϕ, $\pi+\phi$ is the angle between the asymptotes and $\frac{1}{2}(\pi+\phi)$ is the angle of minimum radius.

Thus $\quad\theta = \frac{1}{2}(\pi+\phi)\quad$ when $\quad\cos(\theta\cos\psi)+\sin(\theta\cos\psi)\dfrac{c}{\mathrm{V}}\tan\psi = 0,$

and
$$\mathrm{V}/c\cot\psi = \tan\{\pi-(\cos\psi)\tfrac{1}{2}(\phi+\pi)\}.$$

From the solution of this ψ can be found in terms of ϕ and V/c. It is

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* *Cf.* Sommerfeld's treatment of the elliptical orbit in the theory of the fine-structure of spectral lines, 'Atombau u. Spektrallinien,' chap. 5, § 2.

independent of E. As shown in the previous paper* the correction in the Rutherford scattering formula may be written

$$f^2(\phi, \beta) = \cfrac{\text{cosec}^2\,\psi}{\left\{\cfrac{\beta\,\cot\,\phi/2}{2\,(1-\sqrt{[1-\beta^2]})}\right\}^2}.$$

If the energy is originally written as $\frac{1}{2}m\text{V}^2$, where $m = m_0(1-\beta^2)^{-\frac{1}{2}}$, the correction is

$$\frac{\text{cosec}^2\,\psi}{1/\beta^2(1-\beta^2)\cot^2\,\phi/2}.$$

Some values of $f^2(\phi, \beta)$ are given below—

V/c = β.	φ.	$f^2(\phi, \beta)$.
0·851	2·4° 6 8 10 25	1·79 1·81 1·92 2·09 2·25
0·708 0·851 0·924 0·944	19	1·59 2·09 2·66 2·91

The last part of the third column shows that measurements on the variation of scattering with velocity should deviate considerably from the relation obtaining on the simpler theory. These will now be considered.

The Variation of Scattering with Energy.

Equation (1) $\rho = \frac{1}{4}\pi nt\, b^2 \cot^2\frac{1}{2}\phi\, f^2(\phi, \beta)$ for this case can be written in the form

$$t_m :: \frac{[\text{Energy}]^2}{f^2(\phi, \beta)}\ \text{if the energy is expressed as}\ m_0 c^2\left(\frac{1}{\sqrt{(1-\beta^2)}}-1\right),$$

or
$$\frac{[\text{Energy}]^2}{f^2(\phi, \beta)\,t_m} = \text{const.} \tag{3}$$

Column 8 of the Table below shows that for the measurements made on aluminium, and given in fig. 7, this relation holds within the error of experiment. This is strong evidence for the correctness of the argument in the preceding section, as may be seen by comparing with column 6, in which the relativity correction is omitted. The latter omission, however, amounts to writing for equation (4)

$$\frac{1}{2}m'v^2 = \frac{\text{E}e}{r} + m_0 c^2\left\{\frac{1}{\sqrt{(1-\text{V}^2/c^2)}}-1\right\}$$

which is indefensible.

* *Ibid.*, p. 540.

It is, however, interesting to notice that, if the energy of the particle is written as $\frac{1}{2} m_0 (1-\beta^2)^{-\frac{1}{2}} v^2$, the relation energy$^2/t_m$ (column 7) is very nearly constant. This explains why previous observers[*] have found the formula mentioned to fit their results. For, under the conditions of these and previous experiments,

$$\frac{E^2}{f^2(\phi, \beta)} = E' \text{ within about 20 per cent.,}$$

where $E = m_0 c^2 \left\{ \dfrac{1}{\sqrt{(1-\beta^2)}} - 1 \right\}$ and $E' = \frac{1}{2} m_0 (1-\beta^2)^{-\frac{1}{2}} V^2$.

The conclusion, which must be regarded as accidental, that if the complete relativity expressions for the energy and the orbit are used, the result numerically is almost the same as in the earlier and simpler form, only holds approximately and should fail with slower rays and larger angles of deflection.

Aluminium.

1.	2.	3.	4.	5.	6.	7.	8.
$H\rho$.	E volts $\times 10^{-5}$.	E' volts $\times 10^{-5}$.	$f^2(\phi, \beta)$.	t_m.	E^2/t_m.	E'^2/t_m.	$E^2/f^2(\phi, \beta) t_m$.
				cm.			
1694	2·11	1·80	1·59	0·0010	4·45 . 10^{-6}	3·23 . 10^{-6}	2·80 . 10^{-6}
2742	4·59	3·48	2·09	0·0038	5·55	3·19	2·65
4101	8·23	5·68	2·66	0·0090	7·52	3·59	2·82
4842	10·3	6·80	2·91	0·0124	8·57	3·73	2·93

ALUMINIUM 19°
A.... 10·3 10^5 volts
B.... 8·23 ......
C ... 4·59 ......
D.... 2·11 ...
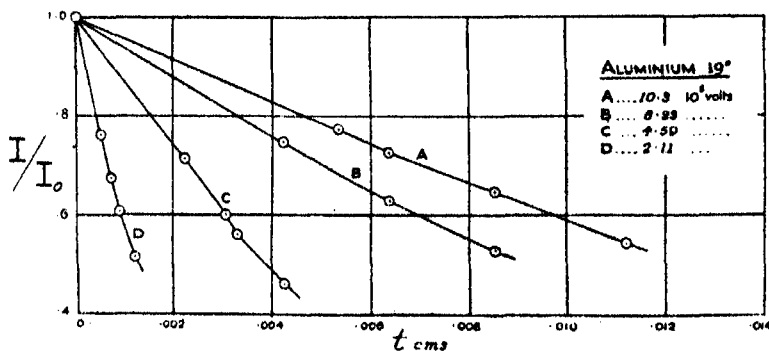
Fig. 7.

A similar variation with velocity was found in a number of experiments made with gold and platinum, but owing to the complication discussed in Section 4, the results are not as simple as for aluminium. A number of

* Crowther, 'Roy. Soc. Proc.,' A, vol. 84 (1910); Geiger, 'Zeit. für Physik,' vol. 6 (1921).

careful determinations gave values for the scattering by platinum which, suitably compared, agreed within a few per cent. with the figures for gold.

§ 6. *Summary of Results.*

The experiments described, together with those of Crowther and the writer, lead to the following conclusions :—

1. The scattering of β-particles observed is a single scattering phenomenon, due to collisions with the nuclei of the atoms encountered.

2. The relations following from Rutherford's theory of single scattering are in general obeyed, though a correction due to the increase of mass with velocity is necessary in the case of the β-particle.

3. Evidence for this correction has been found in the variation of scattering with velocity.

4. The anomalous behaviour of the heavier elements described in the previous paper has been traced, and an explanation based upon the screening action of the electrons surrounding the nucleus appears to be satisfactory.

5. The sources of error in the form of apparatus used have been examined, and absolute numerical values for the scattering found which are in satisfactory agreement with the theory.   It may be added that (4) offers direct evidence for the approximate position and distribution of the electrons immediately surrounding the nucleus.   From (3) and § 5 it is concluded that the law of force in these collisions is that of the inverse square, within from 10^{-11} or 10^{-10} cms. of the nucleus of an atom.

My grateful thanks are due to Sir Ernest Rutherford for his encouragement and guidance in this research.   I am much indebted to Mr. G. R. Crowe for his help in preparing the emanation tubes.

A Study of the Presence or Absence of Nitrogen Bands in the Auroral Spectrum.

By Lord Rayleigh, F.R.S.

In a previous paper* I showed that the negative bands of nitrogen were actually stronger than the green aurora line on the occasion of the auroral display of May 13–14, 1921, which was a typical aurora, in the sense that it was accompanied by conspicuous solar and magnetic disturbance. In contrast with this, the nitrogen bands were not observed at all in the numerous photographs which showed the green line in the night sky on ordinary nights in the south of England.† The point deserved much closer scrutiny, as it might be expected to throw light on whether the ordinary night sky effect was to be classed with the northern lights or not.

To get additional evidence, I proceeded to Shetland in mid-October, 1921. Dr. G. C. Simpson, F.R.S., and Dr. A. Crichton Mitchell very kindly gave me facilities for working at the meteorological observatory near Lerwick, and Mr. J. Crichton, the officer in charge, did everything possible to help, and continued the exposures throughout the winter after I had left. Indeed, all the most successful photographs were taken by him, and forwarded to me for discussion.

The northern lights were several times seen, but, in view of the apparently considerable visual intensity, I was surprised to find how faintly the green line came out with a pocket spectroscope, or on the photographic spectra. I suspect that much of the light is continuous background, which is lost when spread out by the prism.

There is some confirmation in observations with colour filters. Thus, on October 21 there was a bright auroral arch in the north, extending to an altitude of about 30°. It was visible through the orange Wratten filter No. 23, which cuts out the green aurora line. On the other hand, it was not visible through the red filter No. 29, which transmits the red aurora line. It must therefore come from a region of the spectrum between the green and red lines, and since no auroral line is well established to exist in this region, the light is probably to be referred to a continuous background of the spectrum.

The changeable weather in Shetland, with the incessant storms of wind

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* 'Roy. Soc. Proc.,' A, vol. 101, p. 114 (1922).
† 'Roy. Soc. Proc.,' A, vol. 100, p. 367 (1922).

and rain, is very unfavourable to continuous observation. None of the photographs were equal in intensity to the photograph I obtained in the South of England of the world-wide aurora of May 14, 1921.

Those Shetland photographs which showed the green aurora line usually showed the nitrogen bands as well: but less strongly than the green line. In this respect the Shetland photographs stand between those of the world-wide aurora of May 13–14, 1921, and the ordinary night sky in the South of England.

Coming to the latter, the photographs discussed in the former paper* were somewhat faint, few if any of them being robust enough for satisfactory reproduction. It is a question of some importance to determine whether or not nitrogen bands are ordinarily present in the night sky, and for this purpose I made a cumulative exposure at Terling, Essex, with one of the spectrographs mentioned in the former paper (objective aperture F/1·9) for fifteen nights around the time of new moon. All the hours of darkness were utilised from November 21 to December 6, 1921, aggregating about 180 hours.

The green aurora line came up strongly, and besides this there was a faint solar spectrum, showing the band near G, and the H and K lines of calcium. As the moon was not below the horizon during the whole time of exposure, the possibility that this latter was due to moonlight is not excluded.

There was no trace on this plate of the nitrogen bands, and it is certain that their intensity cannot have been more than a very small fraction of the intensity of the green line. The plate used was an Imperial orthochromatic.

Another exposure was made on an Ilford panchromatic plate from December 23 to January 4 inclusive. It showed the green line but faintly, as might be expected from the poor sensitivity in this region. There was no trace of anything else. In particular, there was no solar spectrum, no nitrogen bands, and no trace of the red aurora line.

The search for nitrogen bands could scarcely be pushed much further with this instrument. Exposures have, however, been made with two instruments of much greater light gathering power, working at F/0·9. With these, strong impressions of the green line are sometimes obtained in one clear night: but in no case have the nitrogen bands been detected.

For satisfactory comparison with the Shetland photographs, it is necessary to have at least equal intensity in the green line: only so does the absence of nitrogen bands from the Terling photograph have definite significance. I

* 'Roy. Soc. Proc.,' A, vol. 100, p. 367 (1922).

have selected the more intense Terling photographs for comparison with Shetland, assigning intensities on a scale 1 to 5. It will be understood that if, *e.g.*, a Terling photograph is assigned a density 4 for the green line, the image of that line is actually of about the same density as that of a Shetland photograph marked 4.

It is difficult to give comparable figures for the Terling spectra of May 13–14, 1921 (the occasion of the great magnetic storm), because in this case the various groups of nitrogen bands had their second and third and even fourth heads developed, whereas the first heads were alone visible in the Shetland photographs. It will suffice to recall that the first head of the violet group λ 4278 and the head of the ultra-violet group 3914, each

Shetland Spectra.

Date.	Intensities.				Remarks.
	Green line. 5578.	Nitrogen.			
		Blue. 4709.	Violet. 4278.	Ultra-violet. 3914.	
January 16, 1922 ...	5	1	3	3	Somewhat masked by moonlight.
December 26, 1921 ...	4	0	2	2	
December 24, 1921 ...	3	0	1	1	
December 8, 1921 ...	2	0	1	1	
January 8, 1922 ...	2	0	1	3	
December 28, 1921 ...	2	0	1	2	
December 27, 1921 ...	2	0	0	0	
December 23, 1921 ...	1	0	0	0	

Terling Spectra.

Date.	Intensities.				Remarks.
	Green line. 5578.	Nitrogen.			
		Blue. 4709.	Violet. 4278.	Ultra-violet. 3914.	
Nov. 21–Dec. 6, 1921	5	0	0	0	Cumulative exposure, F/1·9 instrument.
February 17–20, 1922	5	0	0	0	Cumulative exposure, F/0·9 instrument.
February 6, 1922 ...	4	0	0	0	F/0·9.
Feb. 25–Mar. 3, 1922	4	0	0	0	Cumulative exposure, F/0·9.
March 6, 1922 ...	4	0	0	0	F/0·9.
March 8, 1922 ...	4	0	0	0	F/0·9.
March 9, 1922 ...	3	0	0	0	F/0·9.
February 17, 1922 ...	3	0	0	0	F/0·9.

had a somewhat greater photographic intensity than the green line. For further details the Table in 'Roy Soc. Proc.,' A, vol. 101, p. 116, 1922, may be consulted.

No direct comparison of intensity for equal exposure at Terling and Shetland can be given. The uncertain weather in Shetland makes it an unfavourable locality for examining the general light of the night sky, apart from the visually distinguishable aurora which is usually only seen low down in the north.

The comparison I am able to give is between the latter and the general light of the sky at Terling, and it deals only with the intensity of the nitrogen bands relative to the green line. The northern lights in Shetland have a much greater absolute intensity, but it is seldom that a long exposure upon them can be secured.

Calculation of a Primary Standard of Mutual Inductance of the Campbell Type and Comparison of it with the Similar N.P.L. Standard.

By D. W. DYE, B.Sc., A.C.G.I.

INTRODUCTORY.

The standard mutual inductance devised and designed by Mr. A. Campbell and constructed in 1907–8[*] at the National Physical Laboratory has been one of the foundations of our alternating current measurements since that date.

It will be sufficient here to note that the special feature in the design of the Campbell type of mutual inductance consists in a primary single-layer winding, so proportioned that the field due to it is practically zero over the region occupied by the secondary coil. By this means the dimensions of the secondary coil are rendered relatively unimportant, so that it may be an overwound many-layer winding, whereby a suitably large value of mutual inductance may be obtained.

[*] A. Campbell, 'Roy. Soc. Proc.,' A, vol. 79, p. 428 (1907).

A number of fundamental measurements have also been made with its help, including a determination of the ohm[*] and a comparison of self-inductance standards of the Physikalische Technische Reichsanstalt.[†] These measurements give, through various links, an independent check on the accuracy of our standard. From general considerations of the probable accuracy which might be assigned to all the measurements it appeared possible that the uncertainty of knowledge of the value of this standard might be as great as 1 part in 10,000, *i.e.*, considerably greater than the uncertainty which would be assigned to it from the calculations and length measurements. These latter together might amount to 2 or 3 parts in 100,000.

When, therefore, a similar standard of mutual inductance for the Japanese Government, which was under construction by Mr. R. W. Paul, was approaching completion and had shown great uniformity of the spiral groove finally cut on the marble cylinder at the Laboratory, it was thought that highly accurate measurements should be made of the diameter and pitch of the primary winding and also of the mean diameter and cross-section of the secondary winding in order that the value of the mutual inductance of this standard might be calculated to at least as great accuracy as the original N.P.L. standard. With this end in view the primary winding was done at the Laboratory in order that the necessary measurements of the diameter of the bare copper wire under the tension of winding, might be made. The secondary winding was also carried out at the Laboratory in order that the mean diameter of the successive layers of it might be measured as accurately as possible. The calculations were made to the highest accuracy and the full corrections made for departure from mathematical exactness of the actual coils as measured.

The construction of this new standard differs only in minor details from the Laboratory standard; it is not thought that these details can have any measurable effect on the actual value as calculated.

WINDING OF THE PRIMARY AND SECONDARY COILS AND GENERAL REMARKS REGARDING THE NEW MUTUAL INDUCTANCE.

The marble cylinder was sent to the Laboratory for measurement in October 1913, and as a result of the report on these measurements, it was decided to have the two spiral grooves recut and rewound at the laboratory. This, owing to the war, was delayed until the early part of 1920. It was then taken in hand by the Engineering Department who recut the spiral and

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[*] A. Campbell, 'Roy. Soc. Proc.,' A, vol. 87 (1912).
[†] 'N.P.L. Report,' p. 44 (1914–15).

rewound the two coils forming the primary winding. The dimensions and numbers of turns of the two primary windings are as follows :—

Approximate diameter	30 cm.	
Length of coil	7·5 „	
Distance between inside turns of coils	15 „	
Number of turns in each coil	75	

Some time after winding the primary coils, the cylinder was handed over to the Metrology Department and measured according to the scheme detailed below in Section 3 of this paper.

The secondary winding, which is a ring-shaped coil of many layers, was carried out in the Electrical Measurements Department. It is necessary to know the mean diameter represented by the central filament of the cross-section of the secondary, and since this winding consists of twenty layers of silk covered wire with a layer of paper between each, it was thought that the diameters of the central layers might be reduced slightly by the compression of the outer layers. The diameters of each successive layer can only be accurately measured at the time of winding it, before it is subjected to the compression of the outer layers.

In order to get an idea of the possible change in diameter of the layers due to this cause, holes were cut in the cheeks of the ring-shaped marble bobbin at the ends of three diameters spaced 120° apart. These holes allowed the outer wires in each layer to be seen and to be measured by means of a microscope after the whole coil had been wound. The outer wires at each side of the tenth layer were measured through these holes at the time of winding it and again after the whole twenty layers had been wound. The difference between the mean of the six measurements before and after winding the outer ten layers was within the experimental accuracy of the measurements, being less than 0·01 mm.

It may be taken, therefore, that the mean diameter as deduced from the diameters of each layer at the time of winding it represents accurately the mean diameter of the whole winding.

The bottom of the groove in the marble ring was too small to allow the secondary winding to be wound directly on it of the correct mean diameter. A single layer of wire of suitable diameter was, therefore, first wound on and a single layer of paper put over it in order to bring the inside diameter of the secondary winding to such a value as to give the correct mean diameter of the whole coil as nearly as could be determined beforehand.

The finished winding consists of twenty layers of double silk covered wire; each layer has twenty-four turns and there is a strip of paper about 0·08 mm.

thick between each layer of wire. The odd five turns are in a twenty-first layer wound close together near the cheek of the ring at which the ends come out.

The winding is in four sections having the following numbers of turns, 96, 144, 144, 96 + 5 turns, thus making 485 turns in all when in series.

LENGTH MEASUREMENTS OF THE JAPANESE STANDARD.

(1) *Primary Winding on Marble Cylinder.*

(a) *Description.*—The two windings are referred to as P and Q throughout this paper, in accordance with the diagram, fig. 1, which also indicates the system of numbering adopted for the turns. The top of the cylinder is that end at which the outgoing leads are attached. The overall dimensions of the marble cylinder are :—

FIG. I.

Primary windings of mutual inductance.
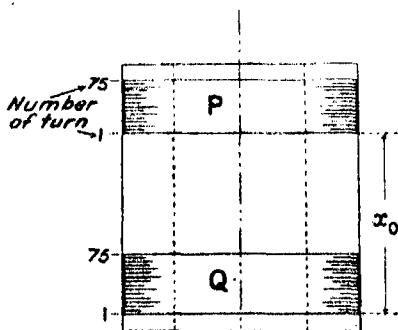
Height .... 35 cm.
Outside diameter ...... 30 „
Inside diameter ...... 18 „

Each coil consists of seventy-five turns of bare wire, having a nominal pitch of 1 mm. and a nominal diameter of 30 cm. The distance x_0 is nominally 22·5 cm.

(b) *Measurement of Diameters.*—The diameters over the wires have been compared with the length of the Laboratory 300 mm. Hartmann Spherical-ended gauge. The variations in diameter are shown in fig. 2. The continuous portions of the curves, together with the extreme end points, are plotted from the calculated means of readings taken six at a time. The dotted lines completing the curves are partly estimated means.

It will be noted that the first turn of coil P has a diameter about 0·1 mm. less than that of the rest of the winding. This is due to the fact that the groove for this turn was added some time after that for the other turns, with the consequent error noted. The method used in the calculations for correction of variation of diameter takes quite accurate account of this comparatively large local variation in diameter.

The final mean diameters over the wires thus found were :—

Coil P = 300·778$_7$ mm. at 17° C. (omitting first turn)
Coil Q = 300·806$_9$ mm. at 17° C.
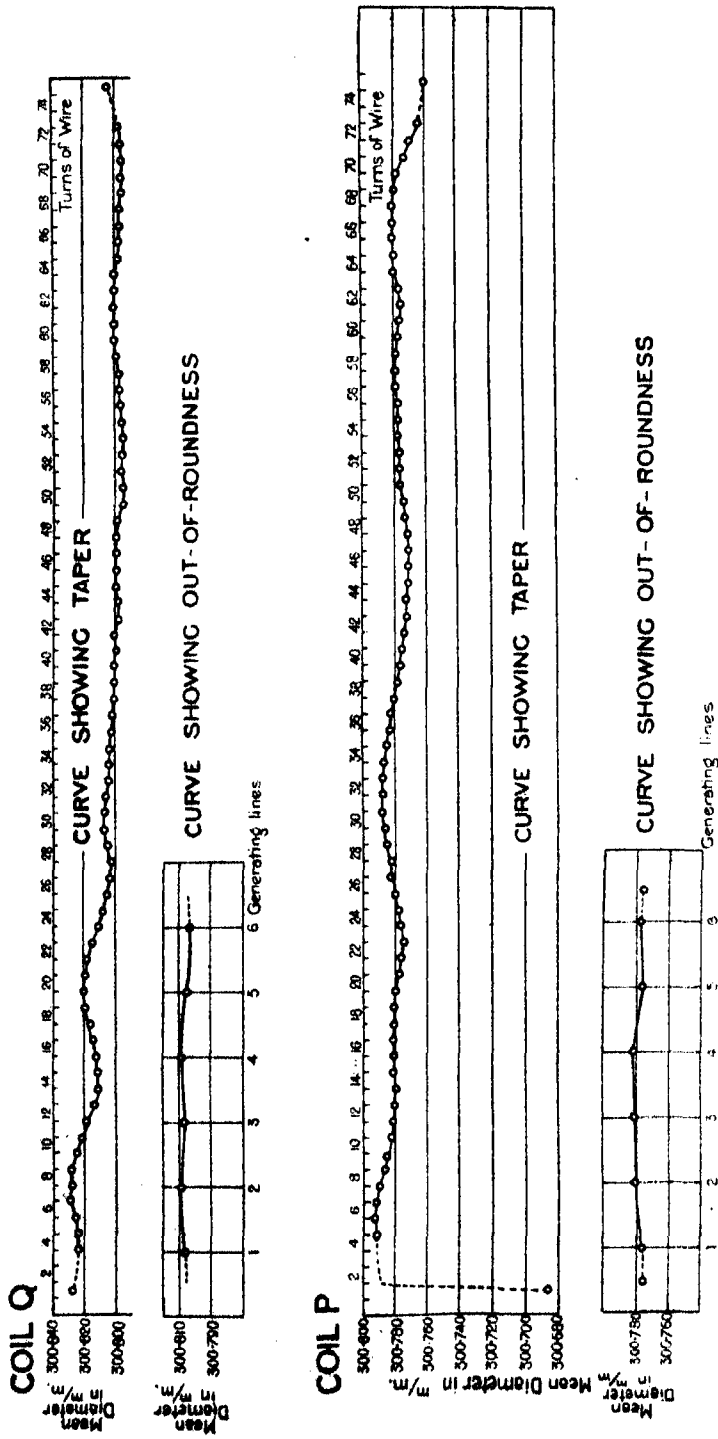
FIG. 2 . MEAN DIAMETERS OF PRIMARY COILS OF STANDARD OF INDUCTANCE

In order to avoid fractional parts in the differences between the true diameter of each turn and the mean diameter, as given above, nominal mean diameters have been used having the values

Coil P = 300·779 mm.
Coil Q = 300·807 mm.

The differences between these nominal diameters and the actual diameter have been read off from the curves of fig. 2, and are given in Section (4), dealing with the corrections for variations from a perfect spiral.

(c) *Diameter of Wire.*—The diameter of the wire was measured at about 100 points for each coil, while it was under tension during the process of winding the wire on the cylinder. The mean diameters of wire thus found were

Wire on Coil P = 0·620$_8$ mm.
Wire on Coil Q = 0·621$_0$ mm.

(d) *Measurement of Pitch.*—The pitch has been measured against the Laboratory line standard Invar No. 27, whose calibration is accurately known. The nominal pitch is 1 mm., and the nominal mean distance from a point on coil P to the corresponding point on coil Q has been taken as 225·445$_8$ mm. All measurements on both coils are reckoned as from the first turn of coil Q, that is, readings on this turn are taken as correct. The nominal reading on any other turn minus the observed reading gives the variation from nominal pitch. These variations are shown in fig. 3. The continuous portions of the curves, together with the end points, have been plotted from the calculated means of readings taken six at a time, and the dotted portions completing the curves are partly estimated means.
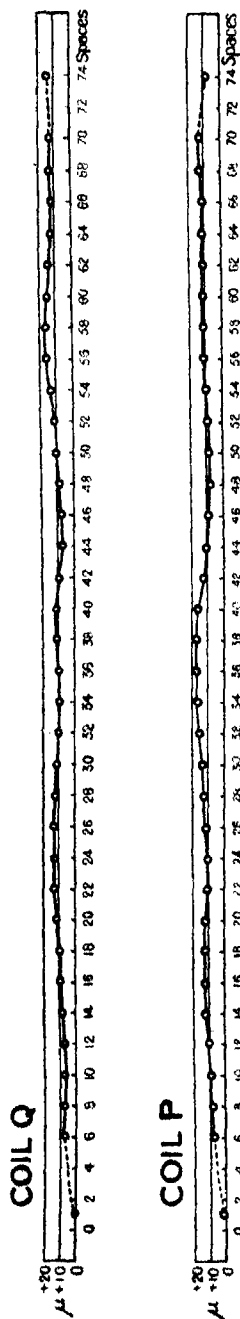
FIG. 3.

MEAN VARIATIONS OF PITCH OF THE PRIMARY COILS OF STANDARD OF INDUCTANCE

COIL Q

COIL P

In order to correct for these variations in pitch, a zero line of $(+10\,\mu = 0\cdot01$ mm.) has been chosen for each coil, and the axial displacements of every wire from the perfect spiral were taken from this base line: these, when multiplied by the appropriate dM/dx at that place, give the desired corrections. The change of the zero line for this purpose makes no difference in the fundamental calculations so long as the same change is made in both coils.

(e) *Irregularities at the Ends of the Windings.*—The ends of the windings come through small ivory plugs of 5 mm. diameter, which are let into recesses in the marble. The surfaces of these plugs are below the surface of the marble; the wires consequently become chords instead of arcs of circles when passing over this space, and the end of the last turn also bulges outwards somewhat before the wire bends sharply in entering the hole in the plug. A calculation of the effects due to this departure from perfection of shape shows, however, that it is quite negligible. The change in mutual inductance due to a change in diameter of $0\cdot2$ mm. of one whole turn of the primary winding is of the order of $0\cdot1$ microh., *i.e.*, 1 part in 100,000 of the total mutual inductance.

There are also local irregularities of pitch near the ends of the windings: these also are of negligible effect.

(2) *Secondary Winding.*

The principle of the Campbell design of mutual inductance is such that the dimensions of the secondary winding are comparatively unimportant. They are, however, sufficiently important to warrant some care in the measurements of mean diameter and dimensions of cross-section of the winding.

The outside diameter of each layer was measured on diameters 120° apart by means of a large micrometer gauge, which was then immediately calibrated against a 17-inch standard spherical-ended gauge. The diameter of the silk-covered wire was also measured at a number of places during winding. The deduced values of mean diameter for each layer are given in Table I, p. 322.

The mean diameter for the whole coil is thus $437\cdot62_5$ mm. The mean diameter, as measured through the holes by microscope, was $437\cdot63$ mm. Since accuracy to $0\cdot01$ mm. in diameter is more than sufficient for an accuracy of 1 in 10^6 in the calculations, the mean diameter has been taken as $437\cdot630$ mm.

> The axial width of winding $=$ Mean of six measurements through the
> holes in the marble ring $= 10\cdot1$ mm.
> Radial depth of winding $= 9\cdot6_8$ mm.

Table I.—Mean Diameters of Successive Layers of Secondary Winding.

Layer.	Mean diameter.	Layer.	Mean diameter.	Layer.	Mean diameter.	Layer.	Mean diameter.
	mm.		mm.		mm.		mm.
1	428·35₄	6	433·28₅	11	438·10₀	16	442·95₀
2	429·34₄	7	434·26₂	12	439·08₆	17	443·91₀
3	430·33₇	8	435·21₀	13	440·02₀	18	444·90₀
4	431·31₀	9	436·18₀	14	440·99₀	19	445·90₀
5	432·28₉	10	437·17₀	15	441·98₀	20	446·91₀

(3) *Measurement of Thermal Coefficient of Expansion of the Marble.*

This was measured at temperatures ranging from 13° to 25°, and found
to be

$$+ 0.000005_9 \text{ per } 1° \text{ C.}$$

(4) *Calculations and Corrections.*

The accurate formula of J. Viriamu Jones was used in the fundamental
calculations. This formula gives the mutual inductance between a circle
and a co-axial helix, having one end in the plane of the circle. A con-
venient form of this formula* is

$$M = 2\pi n_1 (A + a) \left\{ c/k \left(F(k) - E(k) \right) + \frac{A - a}{x} \psi \right\}, \tag{1}$$

where A = radius of circle, a = radius of helix, x = length of helix,
n_1 = number of turns in the length "x" of the helix.

$$k^2 = \frac{4Aa}{(A+a)^2 + x^2} = \sin^2 \gamma. \qquad c^2 = \frac{4Aa}{(A+a)^2}.$$

F(k) and E(k) are complete elliptic integrals of the first and second kinds.
They were computed by formulas (5) and (6),

$$\psi = F(k) . E(k_1' \beta) - [F(k) - E(k)] F(k_1' \beta) - \frac{\pi}{2}$$

in which F($k_1' \beta$) and E($k_1' \beta$) are incomplete integrals of the second kind to
modulus k' and amplitude β

$$k' = \cos \gamma \quad \text{and} \quad \beta = \sin^{-1} c'/k'; \qquad c' = \sqrt{(1 - c^2)}.$$

The values of mutual inductance obtained by the above formula have been
multiplied by 485 in every case so as to refer them to a secondary winding of
that number of turns.

The calculations have been made in two parts, one for coil P and one for
coil Q. The complete curve showing variation of mutual induction with

* A. Campbell, 'Roy. Soc. Proc.,' A, vol. 79, p. 434 (1907).

variation in diameter of the secondary winding, has only been made in the case of coil P. It was not essential to obtain the curve shown in fig. 4, but it forms a most valuable check on the calculation of M for the point required and also checks the curve shown in fig. 5 for dM/dA.

The dimensions used in the calculations for coil P were $a = 15\cdot00791$ cm., $x_1 = 15\cdot0223$ cm., $x_2 = 7\cdot5223$ cm.

Five values of A were taken, viz., $21\cdot3915$, $21\cdot6915$, $21\cdot8815$, $22\cdot0915$ and $22\cdot3915$. The reason these values of A were chosen was that it was thought
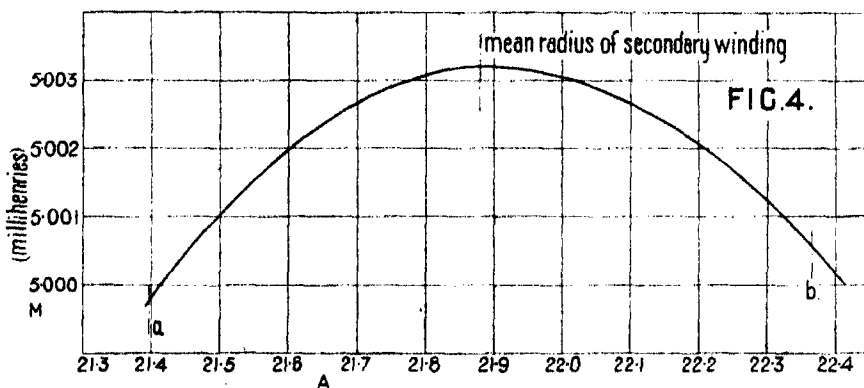
Variation of mutual inductance for variation of diameter of secondary circle.

that the maximum point would be at a radius of A equal to $21\cdot8915$ cm., this was afterwards found not to be the case.

The values obtained for the mutual inductances are given in Table II.

Table II.—Coil P and Secondary Circle of 485 Turns.

A (cm.).	M (x_1).	M (x_2).	M $(x_1 - x_2)$.
$21\cdot3915$	$13\cdot45049$	$8\cdot45080$	$4\cdot99969$
$21\cdot6915$	$13\cdot31803$	$8\cdot31536$	$5\cdot00267$
$21\cdot8815$	$13\cdot23494$	$8\cdot23175$	$5\cdot00319$
$22\cdot0915$	$13\cdot14390$	$8\cdot14109$	$5\cdot00281$
$22\cdot3915$	$13\cdot01502$	$8\cdot01478$	$5\cdot00024$

The curve connecting A and M $(x_1 - x_2)$ is given in fig. 4. For coil Q the values corresponding to its mean radius of $a = 15\cdot0093$ and the mean secondary radius A = $21\cdot8815$ are,

A.	M $(x_1 = 15\cdot0223)$.	M $(x_2 = 7\cdot5223)$.	M $(x_1 - x_2 = 7\cdot5000)$.
$21\cdot8815$	$13\cdot23758$	$8\cdot23354$	$5\cdot00404$

The sum of the mutuals to the circle secondary for coils P and Q is, therefore, $10\cdot00723$.

For averaging over the space occupied by the cross-section of the secondary winding the formula (2) has been used :—

$$M = M_0 + \frac{1}{a}\frac{dM}{dA}\left(\frac{c^3}{6} + \frac{20\,B^2 C^2 - 9\,C^4}{360\,A_0{}^2}\right) + \left(\frac{B^2 - C^2}{6} + \frac{9\,C^4 - 20\,B^2 C^2}{360\,A_0{}^2}\right)\frac{d^2M}{dA^2}$$
$$+ \frac{10\,B^2 C^2 - 6\,C^4}{360\,A_0{}^2}\cdot\frac{d^3M}{dA^3} + \dots, \quad (2)$$

where $2\,B$ = radial depth and $2\,C$ = axial length of cross-section of the secondary.

In order to determine dM/dA, d^2M/dA^2, etc., the curve connecting dM/dA with A was found by calculation and plotting, using the equation

$$\frac{dM}{dA} = 2\pi n_1 n_2\, ck\left\{F(k) + \left(\frac{A+a}{2ax}\sqrt{([A+a]^2 + x^2)}\right)\psi\right\} \qquad (3)$$

in which the symbols have the same meaning as in equation (1); $n_2 = 485$.

The values obtained for dM/dA in the case of coil P are given in Table III.

Table III.

A.	dM/dA microhenries per centimetre.		
	$x_1 = 15\cdot0223.$	$x_2 = 7\cdot5223.$	$x_1 - x_2 = 7\cdot5000.$
21·3915	−444·11	−458·12	+14·01
21·6915	−438·96	−444·61	+ 5·65
21·8815	−435·67	−436·22	+ 0·55
22·0915	−432·00	−427·22	− 4·78
22·3915	−426·72	−414·74	−11·98

FIG. 5.

$\dfrac{dM}{dA}$ (microhenries per cm.)
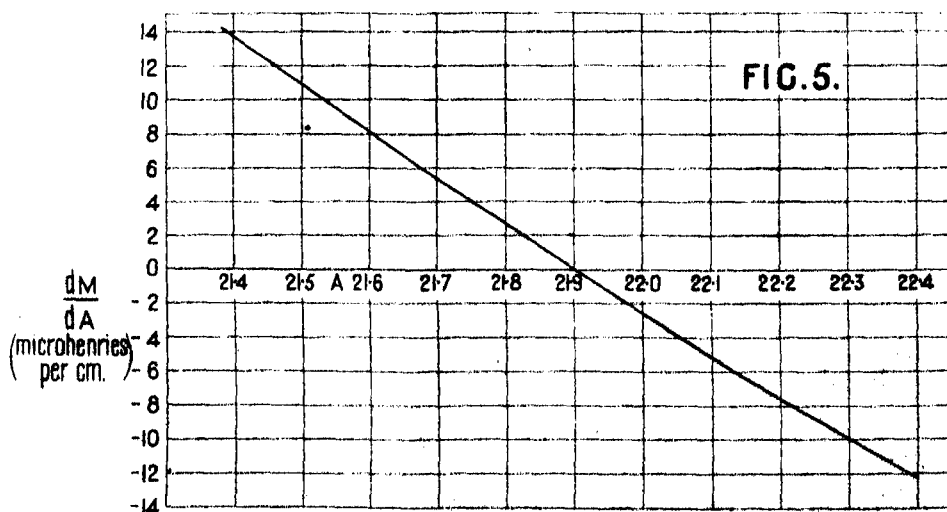
Relation between dM/dA and A for coil P and secondary circle.

The curve connecting A and dM/dA for $(x_1 - x_2 = 7.5000)$ is given in fig. 5. To a sufficient accuracy this curve is represented by the equation $dM/dA = -25.8 \epsilon + 4.5 \epsilon^2$ where ϵ is the difference between any value of A and that value corresponding to the maximum mutual inductance. In the present case A for the maximum mutual inductance, *i.e.*, when $dM/dA = 0$, is

$$A = 21.90_1 \text{ cm. for Coil P, and}$$
$$A = 21.90_4 \text{ cm. for Coil Q;}$$

when ϵ is very small we have, therefore, for the whole mutual

$$\frac{dM}{dA} = -51.6\epsilon, \qquad \frac{d^2M}{dA^2} = -51.6, \qquad \frac{d^3M}{dA^3} = +18.0.$$

In the present case for coil P, $\epsilon = -0.0195$ cm., and $dM/dA = +0.55$; for coil Q, $\epsilon = -0.0225$ and $dM/dA = +0.58$ microh. per centimetre.

The only term of any importance in equation (2) is the term

$$\left(\frac{B^2 - C^2}{6} + \frac{9C^4 - 20B^2C^2}{360A_0^2}\right)\frac{d^2M}{dA^2}.$$

Substituting the values $B = 0.48$ cm., and $C = 0.50$ cm. (allowing for insulation on the wire) we get, for the correction on the total mutual inductance, due to the finite space occupied by the secondary, the result $+0.170$ microh.

We have, therefore, for the case of the mutual inductance with two perfect spirals and a secondary winding of the dimensions given, the value.

$$M = 10.00740 \text{ millih.}$$

Corrections for Axial and Radial Displacements of the Primary Winding.

Each turn of the primary helix is displaced axially and radially from its theoretical position. The most accurate method of determining the corrections due to these displacements is to calculate the dM/da and the dM/dx for each of a number of circles of radius "*a*" and different distances "*x*" from the larger circle A. By plotting these values against x, curves are obtained from which the dM/da and dM/dx for each turn of the primary winding may be read off. These values, when multiplied by the respective displacements radially and axially of each of the turns, give the small corrections on M due to them. The sum of all these corrections gives the total correction to be applied. The dM/da and dM/dx for the circles could have been calculated directly from the formulas for these quantities, but only one more calculation for each point is needed if the actual mutual inductances themselves are calculated; moreover, if the new elegant formulas developed from those for complete elliptic integrals are used for

the computation of the mutual inductances of the circles,* the labour involved is comparatively light, and no tedious and doubtful interpolation in the tables of elliptical integrals is required.

Starting off with the quantities a_0, b_0 and c_0 which have the values given below, Table IV is constructed.

Table IV.

a_0.	b_0.	c_0.
$a_1 = \frac{1}{2}(a_0 + b_0)$;	$b_1 = \sqrt{(a_0 b_0)}$;	$c_1 = \frac{1}{2}(a_0 - b_0)$.
$a_2 = \frac{1}{2}(a_1 + b_1)$;	$b_2 = \sqrt{(a_1 b_1)}$;	$c_2 = \frac{1}{2}(a_1 - b_1)$.
....	....	....
$a_n = \frac{1}{2}(a_{n-1} + b_{n-1})$;	$b_n = \sqrt{(a_{n-1} \cdot b_{n-1})}$;	$c_n = \frac{1}{2}(a_{n-1} - b_{n-1})$.

Then
$$M = \frac{2\pi^2}{a_n}(c_1^2 + 2c_2^2 + 4c_3^2 + \ldots) \qquad (4)$$

"a_0" and "b_0" converge with extreme rapidity to the same value. In general, for the cases under consideration, $a_8 = b_8$ to an accuracy of one part in ten million.

$$a_0 = \sqrt{(A+a)^2 + x^2}; \quad b_0 = \sqrt{(A-a)^2 + x^2}; \quad \text{and} \quad c_0 = \sqrt{(4Aa)}.$$

(*Note.*—c_0 is not required in this formula for mutual inductance.)

The expressions for $F(k)$ and $E(k)$ in terms of the above symbols are

$$F(k) = \frac{1}{2}\frac{\pi a_0}{a_n}, \qquad (5)$$

$$F(k) - E(k) = \frac{F(k)\left[c_0^2 + 2c_1^2 + 4c_2^2 + \ldots\right]}{a_0}. \qquad (6)$$

In computing the values of M for circles, three cases were taken for each value of "x" considered. They were

(1) A, a, x; (2) A, $a + 0.01$ cm., x; (3) A, $x + 0.01$ cm., a.

In these $A = 21.8815$ cm., $a = 15.00791$ cm., and $x = 7.500$ cm.

The difference (2) — (1) gives ΔM corresponding to $\Delta a = 0.01$ cm.

The difference (3) — (1) gives ΔM corresponding to $\Delta x = 0.01$ cm.

In carrying out these computations the constant terms $2\pi^2$ and $n_2 = 485$ have been left out of the calculations till the final additions of the corrections.

The values of M_1, ΔM_1 when $\Delta a = 0.01$ and ΔM_1 when $\Delta x = 0.01$ are given in Table V and curves figs. 6 and 7.

---

* L. V. King, "On some New Formulæ for the Numerical Calculation of the Mutual Inductance of Coaxial Circles," 'Roy. Soc. Proc.,' A, vol. 100, p. 60 (1921).

FIG.6.

ΔM'$\times 10^3$

ΔM' between circles at distance x apart when $\Delta a = 0.01$ cm.

FIG.7.

ΔM'$\times 10^3$

ΔM' between circles at distance x apart when $\Delta x = 0.01$ cm.
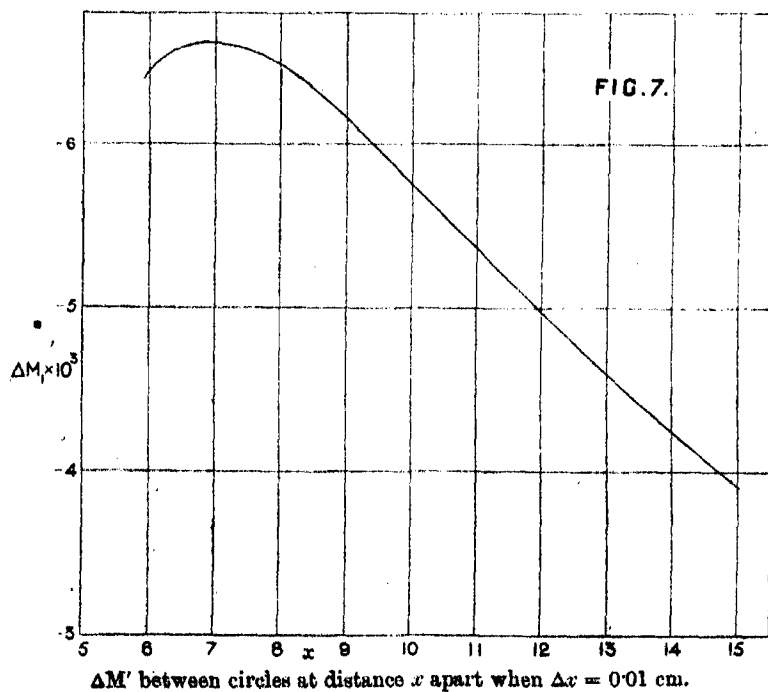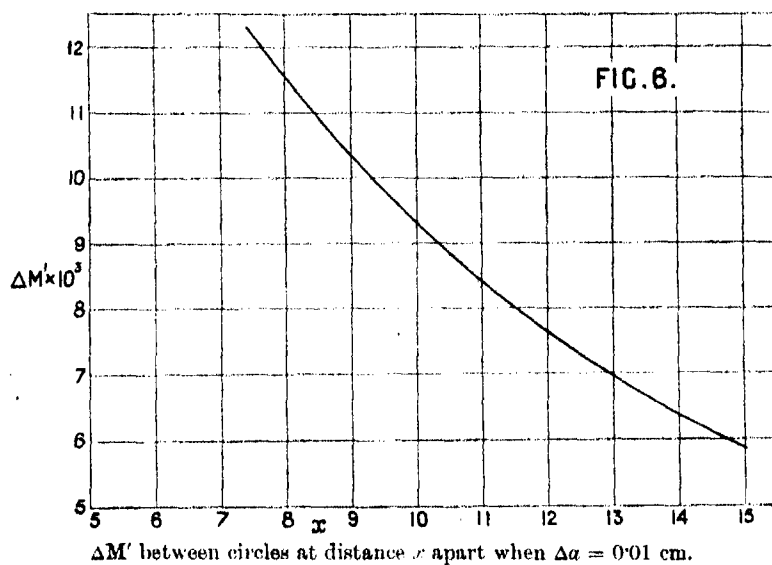
Table V. $M_1 = M/2\pi^2$ for Circles Radii $A = 21\cdot8815$ and $a = 15\cdot0079_1$
with various Values of x.

x.	M_1 (cm.).	ΔM_1 for $\Delta a = +0\cdot1$ mm.	ΔM_1 for $\Delta x = +0\cdot1$ nm.
6·0	10·14853	—	−0·00644
7·5	9·13485	+0·01217	−0·00658
8·0	8·80715	+0·01151	−0·00649
9·0	8·17523	+0·01032	−0·00615
10·0	7·57938	+0·00982	−0·00577
11·0	7·02249	+0·00843	−0·00537
12·0	6·50508	+0·00766	−0·00498
13·0	6·02630	+0·00699	−0·00459
14·0	5·58447	+0·00639	−0·00426
15·0	5·17742	+0·00588	−0·00390

The values of ΔM_1 corresponding to the position "x" of each turn have been read off from these curves and multiplied by the corresponding small differences u and v obtained from the curves, figs. 2 and 3. Since turn 1 on coil P and turn 75 on coil Q are the same distance "x" from the secondary winding, the algebraic sum of their radial and axial differences may be taken when multiplying by ΔM_1. A selection of the results of the calculations is given in Table VI, in which turn 1 now has the position "outer" on both coils and turn 75 the position "inner" on both coils.

Table VI.

Turn.	Sum of radial displacements on P and Q in units of 10^{-3} mm. $= u$.	Sum of axial displacements on P and Q in units of 10^{-3} mm. $= v$.	The unit is $1 = \dfrac{10^{-6} \text{ microh.}}{2\pi^2}$.	
			$u \times \dfrac{dM_1(a)}{dx}$.	$v \times \dfrac{dM_1(x)}{dx}$.
1	+ 1	+ 9	+ 5·9	− 85·0
5	+10	+ 7	+ 61·2	− 28·2
10	+17	+ 6	+ 108·3	− 25·2
15	+ 1	+ 4	+ 6·6	− 17·5
20	+12	0	+ 85·6	0
25	− 4	− 6	− 29·1	+ 28·5
30	− 7	− 3	− 53·3	+ 14·8
35	− 8	+ 6	− 63·9	− 30·7
40	− 3	+ 5	− 25·1	− 26·6
45	+ 2	+ 7	+ 17·6	− 38·4
50	− 8	+ 1	+ 74·2	− 5·7
55	−12	− 4	− 117·4	+ 23·7
60	− 4	− 4	− 41·2	+ 24·4
65	− 7	− 4	− 66·0	+ 25·1
70	+ 2	− 8	+ 22·9	+ 51·6
75	−97	−14	−1178·5	+ 92·0

The whole correction for the seventy-five turns of both windings of the primary was found to be—

> For radial displacements of the wires $= -0.084$ microh.
> For axial   „   „ $= +0.015$ „

CORRECTION FOR THE FIVE TURNS FORMING THE TWENTY-FIRST LAYER.

The calculations relative to averaging over the cross-sectional area occupied by the secondary winding assume the whole of it to be contained within the rectangle formed by the twenty layers of twenty-four turns each; the extra five turns necessary to obtain the mutual inductance of 10 millih. are wound close together near the upper cheek of the ring. They may, to a sufficient accuracy, be considered as equivalent to a five-turn circle displaced radially by $+0.5$ cm. and axially by 0.4 cm. from the central filament of the secondary winding.

The corrections due to these displacements are :—

> For axial displacement $= +0.041$ microh.
> For radial   „ $= -0.061$ „
> Net correction $= -0.020$ „

There is, finally, a correction due to one of the coils having slightly more than seventy-five turns; the overlap is 1·2 mm. If the outgoing leads are close together, this extra piece may be considered as equivalent to a positive mutual inductance due to the part NP (Fig. 8) of the circle at one end of the helix together with a negative mutual given by the very open spiral QP formed by the outgoing lead from the end Q. QN is a generator of the cylindrical surface of the winding.

If the piece NP is considered as at the end of the helix closest to the secondary winding, the positive mutual inductance due to it will be greater than the negative mutual inductance due to the return lead QP; on the other hand, if the small piece is considered as at the end, Q, of the helix its positive value will be less than the negative value of QP. The length measurements of the distance separating the two helices are not quite sufficiently accurate to determine which case is correct.

FIG. 8.

Appertaining to overlap at one end of helix.

There is an uncertainty, also, due to the return piece QP being on a different cylinder to the helix, owing to the ends Q and P first going radially inwards through the walls of the hollow marble cylinder. The uncertainty introduced

by the ends before they come away together is probably of the order $\pm 3 \times 10^{-6}$.

Summing up the various calculations and corrections we have for the value of the standard,

For perfect Helix P .... $M = 5003 \cdot 19$ microh.

„   „   Q .... $M = 5004 \cdot 04$ „

	Microh.
Correction for averaging over cross-section of secondary	$+0 \cdot 170$
„ for irregularities of diameter of primary helices ...	$-0 \cdot 084$
„ „ pitch of primary helices.........	$+0 \cdot 015$
„ for five turns on outside of secondary winding......	$-0 \cdot 020$

These together give for the final calculated mutual inductance of the standard the value at 17° C.

$$M_{17} = 10 \cdot 0073_1 \text{ millih.}$$

Probable Accuracy of the Calculated Value of the Standard.

There are five factors entering into the calculations, each of which represents a series of length measurements. If a probable accuracy is given to these measurements it is possible to assign a probable accuracy to the final result. The factors involved are—

(1) Diameter of primary helices.
(2) Pitch and distance apart of primary helices.
(3) Diameter of secondary winding.
(4) and (5) Width and depth of secondary winding.

For the present purpose the helices may be replaced by a circle 10 cm. distant from the plane of the secondary winding.

If it is assumed that the diameter is accurate to $\pm 0 \cdot 001$ mm., and the pitch to $\pm 0 \cdot 002$ mm. for the primary winding; also that the mean diameter of the secondary winding is accurate to $\pm 0 \cdot 1$ mm., and the width and depth of the secondary cross-section is accurate to $\pm 0 \cdot 05$ mm., the following will be the resulting uncertainties in M expressed as parts in a million :—

For—Primary diameter.....................	± 6
„ length and distance apart·	± 16
Secondary diameter..................	$\pm 0 \cdot 7$
„ depth and width	± 8 each.

The maximum error is therefore 40 parts in 10^6, but the mean probable error will be of the order 20 parts in 10^6.

Comparison with the N.P.L. Standard Mutual Inductance.

(a) *Calculated Value of N.P.L. Standard.*—The original value calculated from measurements of dimensions made when the N.P.L. standard was first constructed in 1908, was

$$M_{15} = 10.0178_5 \text{ millih. at } 15° \text{ C.}$$

In 1914, it was thought desirable to check the measurements of the standard. The paraffin-wax coating over the primary windings was dissolved off with petrol, and the pitch and diameter of these were again measured in the Metrology Department. It was found that changes in the dimensions had taken place, but whether these were secular, or due to the waxing or subsequent treatment with petrol, it is impossible to say. The diameters of the two helices were about 5 parts in 100,000 greater, and the axial lengths were all about 1 part in 10,000 greater. The net result of these changes was to make the value of the mutual inductance about 7 parts in 10^6 smaller. The value at 15° C., as determined from the second set of measurements, was

$$M_{15} = 10.0177_8 \text{ millih.}$$

Owing to the uncertainties attaching to the effects of paraffin-waxing, it was decided not to wax either of the windings of the new standard. The windings can, therefore, be measured without trouble at any future time.

Comparison.

The two standards were compared by measuring each on a variable mutual inductometer. In order to avoid capacity effects a frequency of 10 cycles per second was used, at which frequency the sensitivity was about 3 parts in a million.

Observations were made alternately, first on one standard and then on the other. Balance on the new standard was, at first, found to be imperfect; this imperfection was traced and found to be due to metal parts in the levelling screws and sockets used to support and adjust the secondary winding. These were replaced by non-metallic parts, and, as a result, the balance was perfect, as far as could be judged on the galvanometer.

The results of four comparisons gave for the difference between the two standards the values

$$10.6_2, \quad 10.7_0, \quad 10.6_3, \quad 10.6_0 \text{ microh.}$$

The mean difference at 16° C. may be taken, therefore, as

$$10.6_4 \text{ microh. } (\pm 0.05 \text{ microh.}).$$

The calculated value of the new standard at 17° C. is

$$M_{17} = 10.0073_1 \text{ millih.}$$

If all the dimensions of a mutual inductance change in the same proportion the value of mutual inductance changes in that proportion also. The coefficient of thermal expansion of the marble of the new standard is $+0.000006$ per 1° C.

The mutual inductance at any temperature "t" will therefore be

$$M_t = M_{17}[1 + 0.00006(t-17)].$$

The N.P.L. standard has the value at 15° C.

$$(\text{N.P.L.}) \; M_{15} = 10.0177_8 \text{ millih.}$$

Correcting the value of the new standard to this temperature we have

$$(\text{New}) \; M_{15} = 10.0071_9 \text{ millih.}$$

The difference between the two calculated values is 10.5_9 microh. The mean measured difference, as given above, is 10.6_4 microh.

This agreement between calculation and measurement may be considered highly satisfactory; it is closer than the various probable errors might lead one to expect.

It appears, therefore, that both these standards are accurate to within about 1 part in 100,000, in their values calculated from the dimensions as measured in terms of the N.P.L. standards of length.

Apparatus for Determining the Standard Deviation Mechanically.

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College, Cambridge.

(Communicated by G. Udny Yule, F.R.S. Received March 6, 1922.)

The calculating apparatus here described is a natural development from
the "harp" harmonic analyser,[*] and similarly makes use of loaded strings,
which apply forces to a flexible yoke, whose consequent movement resolves
these forces automatically. The use of vertical strings in place of the
horizontal ones employed in the "harp" being convenient for the special
purpose of this apparatus, it became possible so to design it as to give quan-
titative amplitudes to the yoke movements, which in the "harp" were only
qualitative.

Purpose of Employment.

The purpose of the apparatus is to enable tolerably precise calculations of
standard deviation and other related statistical constants to be made quickly,
and in the hands of persons other than trained computers. Much of the work
done in any laboratory is necessarily restricted by considerations of time and
labour to the production of figures which in any one set of observations are
not sufficiently numerous to justify laborious statistical treatment. Or,
equally, the known imperfections of material or of method may themselves
result in errors in the computed statistical constant, so that computation of,
e.g., a standard deviation beyond two significant figures would have no real
value. In both cases an approximate determination is all that the circum-
stances warrant, and only then if that determination can be made rapidly by
anybody available. The present apparatus makes this possible.

General Construction.

The complete apparatus is shown in fig. 1. On a 6-foot vertical board are
fastened the yoke-holder with its yoke (fig. 3) and the template-grid (fig. 2).
From the yoke-holder (yh) the yoke (y) is suspended at either end by two
short suspensions of fine cotton tape (typewriter ribbon). At the centre of
the yoke there converges from below a set of twenty-five strings of sewing
cotton (s); of these, the centre one (sb) is stronger than the rest and bears a
"dead load" or "base" weight of 2000 grm. (wb). The other strings to right
and left of this base string bear weights (w) proportionate in succession to

* W. L. B., "A Simple Apparatus for Approximate Harmonic Analysis and for
Periodicity Measurements," 'Roy. Soc. Proc.,' A, vol. 99 (1921).
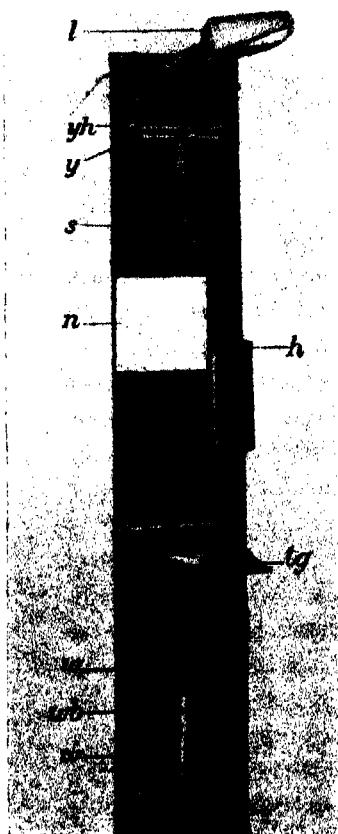
FIG. 1.—General view of standard deviation calculator.
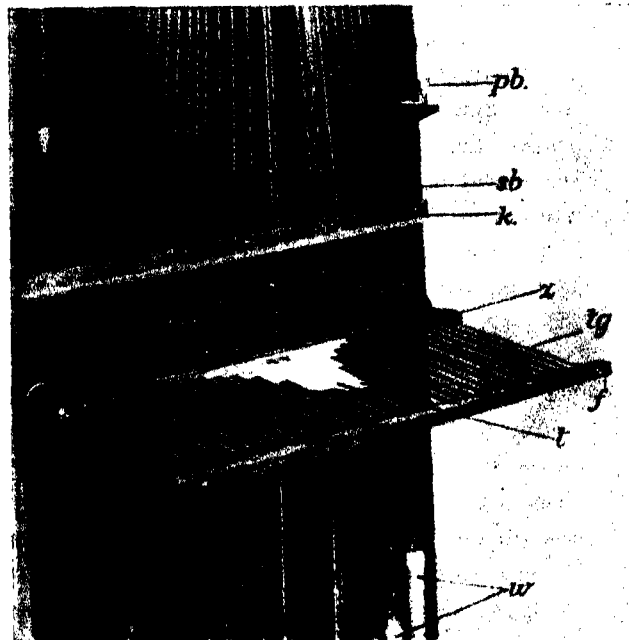
FIG. 2.—The template-grid, with a template in position.
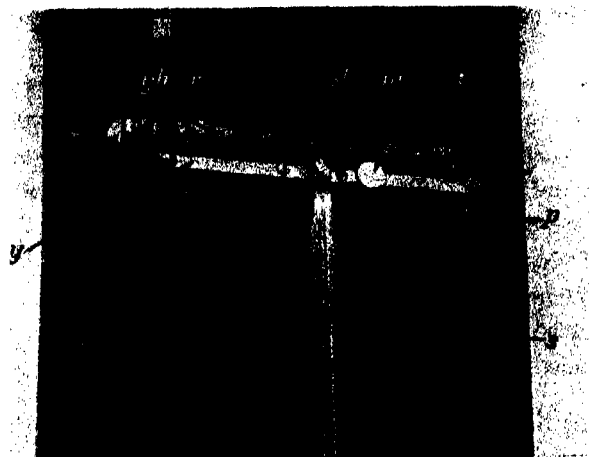
FIG. 3.—The yoke.

the square of their deviation from it. The actual weights, in grammes, on the strings are thus :—

$$
\cdot \quad \begin{matrix} 144 & 100 & 64 & 36 & 16 & 4 \\ & 121 & 81 & 49 & 25 & 9 & 1 \end{matrix} \quad (2000) \quad \begin{matrix} 4 & 16 & 36 & 64 & 100 & 144 \\ 1 & 9 & 25 & 49 & 81 & 121 \end{matrix} \quad \cdot
$$

Each string is retained in its proper place in the series by passing through the template-grid (*tg*), below which the weights (of lead tubing) hang in two tiers, so as not to touch one another. The template-grid consists of two parallel brass bars (*f* and *z*), tied together by a rank of parallel steel rods, these being so arranged that at the grid every string is 1 cm. from its neighbours. The back of the grid is bolted to the base board, and the grid thus also serves as the operating table on which the template (*t*) under examination is laid, the back brass bar (*z*) defining the zero abscissa. The yoke-holder is set back slightly behind the grid, so that the weighted strings rest in contact with the rear brass bar of the grid at the zero for each ordinate of the frequency curve to be examined.

Method of Use.

To use the apparatus, the frequency curve in question is plotted on ordinary squared paper with ordinates 1 cm. apart and abscissæ 0·5 cm. apart. This is then cut out with scissors as a graph or template of rectangular co-ordinates, which is folded lengthwise and balanced on a middle point to find the mean ordinate. A straight-edge is then passed behind all the strings (*s*), excepting the zero string (*sb*), to pull them forward, and the template (*t*) is laid on the grid with its base against the back bar of brass (*z*), the rectangle which includes the mean ordinate being centred on the base string (*sb*). By withdrawing the straight-edge, the strings are allowed to fall back until each one rests on the edge of its appropriate rectangle in the template, or else on the brass bar as before (fig. 2).

The new force now exerted on the yoke in a plane perpendicular to that of the base board by any one string is proportionate, firstly, to the deflection, if any, of that string from its resting position by the template, *i.e.*, the height of its particular ordinate ; and, secondly, if so deflected, to the square of the deviation of the position of that string along the grid from the base string, on account of the weight it carries.

The consequent movement of the yoke is read by a mirror (*m*) attached to it, as in the " harp," a lamp (*l*) fixed at the top of the base board, and a plane mirror (not shown) behind the observer, which reflects the image of the lamp filament upon a hooded scale (*h*) fixed on the base board conveniently for observation.

The movement there observed, which represents the "sum of the squares of the deviations," is quickly corrected for n, the number of points in the frequency, and the square root is also extracted by using a nomograph (n), fastened conveniently on the base board.

Allowing one minute for cutting the template, another minute suffices to complete the whole operation of determining a standard deviation; or $\sqrt{(\Sigma d^2/n)}$, irrespective of whether n is large or small. The result has not been corrected for the deviation of the true mean from the base ordinate chosen, since the correction is small if the standard deviation exceed some two units of the scale. For the true standard deviation σ_0 is related to the root mean-square deviation, δ, about an arbitrary origin by the equations

$$\delta_0{}^2 = \sigma_1{}^2 - e^2$$

where e is the difference between the mean and the arbitrary origin. That is, approximately, if e/δ be small:

$$\sigma_0 = \delta_1 \left(1 - \tfrac{1}{2}\frac{e^2}{\delta_0{}^2}\right).$$

The maximum value of e in our case is $\frac{1}{2}$, so that the maximum value of the correcting term $\frac{1}{2}e^2/\delta^2$ is $1/8\,\delta^2$ if σ is 2, that is 1/32 or 3 per cent. If σ is 3 it is 1/72, or barely $1\frac{1}{2}$ per cent. When the data are being grouped the interval should be so chosen as to make the number of groups approach as nearly as is convenient to the limit for the instrument (25), in order to keep down possible error from this source.

The Design of the Yoke.[*]

In the harp harmonic analyser we employed a light yoke of wire, since the load on its yoke was constant and no great accuracy was needed in measuring amplitudes, which, moreover, embraced only a very small angular movement In the new apparatus we habitually vary the total deflecting load on the yoke over a very wide range, equal sensitivity is required in all parts of the resulting scale deflection, and we further require these deflections to be strictly quantitative at all times. Zero constancy, however, as we had already seen in the harp, could take care of itself in these loaded string constructions. In the first model of the apparatus we used parallel strings, and proposed to obtain the correction for n automatically by inserting the template at

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[*] Our use of the stretched-string construction may perhaps be interpreted as due to inadequate resources, or to lack of knowledge as to the possibilities of precise workmanship and sensitive design; but such is not the case. The resources afforded by the precision machine tools in the Mechanical Section of our Department were discarded deliberately—not on grounds of expense, but on grounds of efficiency, especially in respect of constancy.

proportionate distances from the yoke. This we found inadvisable; in any case, some form of nomograph or special scale would be required to extract the square root, and the operation $\Sigma d^2/n$ might as well be done in the same way: the whole base-board could then be simple. Further, the use of parallel strings subjects the yoke to a turning movement whenever the loading is not symmetrical round the base string; the constraining of the yoke against the rotation presented many difficulties. A bifilar suspension was useless, and on trying a four-fold suspension of the ballistic pendulum type, we met further difficulties.

It should be noted that any suspension material is extensible, that it is impossible to use mechanical connections (cup and vee bearings, etc.) since their frictional resistance may vary or may be excessive in such small angular movements, and, lastly, that construction which depends on accurate workmanship should only be admitted as a last resort. The objections to the ballistic pendulum suspension involved all three considerations; if long suspensions were employed, the method was accurate, but the angular rotation of the yoke, which we desire to measure, was trivial, while the bodily translation of the yoke from zero position brought in fresh corrections; short suspensions were thus inevitable, but these required great exactitude in superposing the upper and lower ends of the four main suspensions, and in the tension-equality of the cross strings. These conditions are impossible of permanent achievement, however much care may be taken in the original construction, since spun threads alone can give sufficient flexibility; the thinnest steel foil has sufficient stiffness to prevent quantitative reactions of the yoke at big deflections under the small loadings, unless impossibly heavy weights are used. The ballistic suspension was therefore abandoned.

We then returned to the divergent strings employed in the harp, again using an angle of divergence sufficiently small to have no appreciable error-effect, and even this can be removed by slightly increasing the weight carried by any one string so as to give the correct vertical component if necessary, but on the balance of minor considerations we consider it inadvisable to do so. A related, though separate, source of error might be expected in the friction of the splayed-out strings on their guides, as also on the template edge; actually, we find that this slight tendency to over-load or under-load any one string is effectively eliminated by vibrations during the setting up of a template and by the flexibility of the paper template itself. The yoke remained at full width, supported at its ends,* and carrying all the strings at its middle (fig. 3). Any tendency to rotation in a horizontal plane was thus reduced to vanishing point.

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* The black typewriter ribbons used for the suspension are scarcely visible in fig. 3. Their positions are indicated by *r r.*

In the early stages we had endeavoured to keep the weight of the yoke as low as possible, but this was obviously absurd, since in a weightless yoke the deflections produced by any weight on a string would be identical, and further the weighted strings themselves loaded the yoke. A base string (*sb*) was therefore added, on which the 2,000 grm. dead load weight (*sw*, fig. 1) hung permanently, thus defining the sensitivity of the apparatus, and rendering it practically independent of the displacements of the other weights, 1 to 144. The yoke could now be made heavy and strong in order permanently to assure two conditions: firstly, that it would never alter during use; and secondly, that one straight line should contain the flexion-points of all the strings, another straight line should contain the flexion-lines of both suspension ribbons, while these two lines should be in one plane and be fairly parallel.

These conditions were sufficiently satisfied by the only piece of machining employed in the apparatus. The yoke was made of two mild steel bars of ¾ inch square section, which were first clamped side by side and milled simultaneously along their upper faces. These milled faces were then opposed to one another, when any errors in the run of the milling cutter were naturally balanced out, the points of actual contact between the faces lying in one plane; and between them the two ribbons and twenty-five strings were simply clamped by bolts running through both bars (fig. 2, *y*).

As a minor precaution the yoke was provided in front with a small adjustable slider (*sl*), and after a 2 cm. concave mirror (*m*) had been fixed on it with wax and the yoke suspended in position, this slider was moved until the yoke balanced in the same position under its own weight as when it carried all the other weights also, totalling 3 kgrm.

It remained to support the yoke, and this was conveniently done by a similar pair of bars (*yh*) to clamp the upper ends of the ribbon suspensions (*rr*), these bars being mounted on two screwed rods projecting from the base-board so that the yoke could be moved in or out till the strings at rest made contact with the zero abscissa, *i.e.*, the back brass bar (*z*) on the template grid.

Two strong pegs (*p*), fixed just below the yoke, serve as safety stops to catch it in the event, not yet realised, of a ribbon suspension breakage. Two plumb bobs (*pb*) assist in fixing the board correctly. A rack (*k*) with slots cut in it is added to take the load of the weights, by means of lead shot clipped on each string, when the instrument is being moved about.

Errors of Observation.

These are insignificant, the chief ones residing in the actual reading of the position of the spot of light, and in reading the nomograph. Slight apparent changes of zero may result from warping of the lamp and plane mirror

supports, or of the wax which secures the concave mirror to the yoke, but these are checked by a glance at the graduated scale before inserting a template. The friction of the strings on the steel rods of the template-grid might cause trouble if the latter were allowed to rust, but is not detectable if a film of vaseline is left on the steel. Internal friction in the typewriter ribbon and sewing cotton is also imperceptible and appreciably invariable.

Advantages of the Apparatus.

The apparatus may safely be set aside for months, with the certainty that it must function as well as ever when required. It gives standard deviations correct to within ± 3 per cent. of the computed value, apart from the base correction, which itself is definitely limited to small dimensions by the method of use. The complete determination of a standard deviation can be made by any person, irrespective of statistical training, and with a marked saving of time. The time required for a determination is largely independent of the amount of calculation required, and the saving of time in comparison with ordinary calculation is thus greater with large arrays than with small ones. Both methods require identical procedure until the frequency curve has been plotted from the original data; after which the time required to obtain the final result was as follows, in three demonstration trials.

The following times were taken in stop-watch trials of the instrument against a practised computer. The computer employed a Burrough's Desk Adder, statistical tables and the slide-rule. Both the computer and the instrument started with the curve plotted, and the value of n known. Trial A demonstrated the superior dependability of the instrument in such hasty work.

(A) Curve with $n = 215$: Standard deviation $= 4.98$.

      (1) Computer's time, 6 minutes. Result entirely incorrect. (Repeated calculation.)

          Computer's time, 8 minutes. Result correct.

      (2) Instrument's time, 3 minutes 5 seconds. Result approximately correct (S.D. $= 4.9$).

Of this trial the detailed timing was as follows :—

	Mins.	Secs.
Cutting template	1	50
Balancing for mean ordinate	—	15
Insertion and reading deflection	—	35
Removal	—	10
Reading nomograph	—	15
Total	3	5

(B) Curve with $n = 35$: Standard deviation $= 2.18$.

This curve was purposely made of a shape inconvenient to manipulate in template form.

Both computer and instrument took 3 minutes with similar results. The detailed timing of the latter was as follows :—

	Mins.	Secs.
Cutting template	1	15
Balancing template	—	25
Insertion and reading deflection	—	45
Removal	—	10
Reading nomograph	—	15
Total	2	50

(C) Curve with $n = 210$: Standard deviation $= 5.68$.

Computer's time, 9 minutes.

Instrument's time, 3 minutes.

The floor space occupied is only $12'' \times 18''$.

The construction can be undertaken at any simply equipped work bench, as even the milling operation on the yoke bars can be replaced by lapping with carborundum.

Table of Test Results.

As a final test for the dependability of the apparatus, seven test templates were prepared, as shown in the following Table, of which Nos. 1 and 4 were particularly stringent tests.

It will be seen that the computed and observed results agree very closely over this wide range of test. It may also be pointed out that the height of the template grid permits of a maximum ordinate of twenty-seven $\frac{1}{2}$ cm. units, and that the sensitivity of the apparatus can be doubled if no more than thirteen-unit ordinates are likely to be met with, since the templates can then be plotted in 1 cm. units.

Conclusions.

The paper describes and illustrates :—

(1) Another calculating apparatus derived from the harmonic analyser formerly described.*

(2) The present apparatus mechanically applies the method of least squares to calculating standard deviations of frequency distributions.

(3) By suitable modifications of the arrangement used in the harmonic analyser, the loaded-string system has been made to give quantitative results over a wide range of amplitudes and weightings.

* W. L. B., *loc. cit.*, p. 286.

Seven Test Templates.

Deviation.	1.	2.	3.	4.	5.	6.	7.	Notes.
−12	—	4	—	—	—	—	—	No. 7 is the template shown in figs. 1 and 2.
−11	—	4	—		—	—	—	
−10	...	4	—	—	—	1		
− 9	—	4	—	—	1	2		
− 8	16	4	4	16	2	3		
− 7	16	4	4	14	2	1		
− 6	16	4	4	12	3	6		
− 5	16	4	4	10	3	5	1	
− 4	16	4	4	8	3	4	3	
− 3	16	4	5	6	4	10	7	
− 2	16	4	4	4	4	6	13	
− 1	16	4	4	2	4	8	17	
0	16	4	4	0	5	6	19	
1	16	4	4	2	5	6	17	
2	16	4	4	4	6	4	13	
3	16	4	4	6	4	6	7	
4	16	4	4	8	4	2	3	
5	16	4	4	10	3	—	1	
6	16	4	4	12	2			
7	16	4	4	14	1	2		
8	16	4	4	16	1	3		
9	—	4	—	—	1	5		
10	...	4	—	—	1	1		
11		4						
12	...	4						
N	272	100	68	144	59	81	101	
$\sqrt{(\Sigma d^2 / n)}$								
(1) Computed ...	4·90	7·20	4·90	6·00	4·45	4·80	1·97	Computed, using 10-inch slide rule.
(2) Observed ...	5·0	7·2	4·9	6·3	4·4	4·8	2·0	Direct reading from apparatus.

(4) The apparatus is simple and inexpensive to construct, simple and quick in use, and retains its sensitivity and zero indefinitely.

On the Structure of the Line λ = 6708 *A. of the Isotopes of Lithium.*

By J. C. McLennan, F.R.S., and D. S. Ainslie, M.A., University of Toronto.

[Plate 4.]

I. *Introduction.*

From considerations based on known similarities between the series spectra of the alkali elements, it was to be expected that the members of the series $\nu = (1{\cdot}5, s) - (m, p)$ for lithium should consist of close doublets.

In 1913 Zeeman[*] investigated the absorption of the wave-length λ = 6708 A., the first member of the above series for this element, and found by the use of a concave grating of high resolving power that it consisted of a close doublet, with an estimated separation of 0·144 A. In the following year, Takamine and Yamada[†] also investigated the structure of this line, and found that it could be obtained in the form of a comparatively sharp doublet, with a separation of 0·165 A. In their experiments the source of radiation consisted of a brush discharge between iron terminals moistened with a 10 per cent. solution of LiCl. The spectral separation was measured with a 35-plate échelon grating.

In 1914 Kent[‡] also investigated the wave-lengths λ = 6708·2 A., λ = 6103·77 A., λ = 4972·11 A., and λ = 4602·37 A., and found by the use of an échelon grating that all four wave-lengths consisted of doublets with the wave-length differences 0·151 A., 0·114 A., 0·084 A. and 0·069 A. respectively. He also found that in weak magnetic fields the members of the doublet λ = 6708·2 were resolved into components of the types given by the sodium lines D_1 and D_2. With strong fields the magnetic resolution of the combined members of the doublet was that of a normal Zeeman triplet.

More recently, in 1916, King[§] made a study of the structure of the lithium red line in the furnace spectrum of the vapour of this element with a ruled grating, and found again that it consisted of a doublet when a small

* Zeeman, 'K. Akad. Wetensch. Amsterdam, Proc.,' vol. 15, pp. 1130–1131 (1913).

† Takamine and Yamada, 'Proc. Tokyo Mathematico-Phys. Soc.,' 2nd Series, vol. 7, No. 18, p. 339 (1914).

‡ Kent, 'Phys. Zeit.,' vol. 15, p. 383 (1914).

§ A. S. King, 'Astrophys. Jour.,' vol. 28, p. 300 (1916).

quantity of lithium was used with a separation of 0·152 A. When high vapour densities were used, however, the line appeared as a triplet of variable separation from 0·25 to 0·36 A. In discussing his results King suggested that this variation in the interval of the triplet possibly originated in electrical resolution such as one obtains in the Stark effect.

Quite recently a study of the structure of the lithium red line was made by the writers by using a vacuum arc in lithium vapour as a source of radiation, and by using both Lummer plates and a 30-plate échelon grating crossed with a Lummer plate to effect the resolution.

In the course of this study it was found that when strong arcs were maintained in the vapour, the wave-length λ = 6708 A. consisted of a close quartet with separations of 0·128 A., 0·173 A. and 0·165 A.

II. *Apparatus.*

The apparatus used for producing the arc which is illustrated in fig. 1 consisted of a brass water-cooled chamber of the type shown in the diagram.
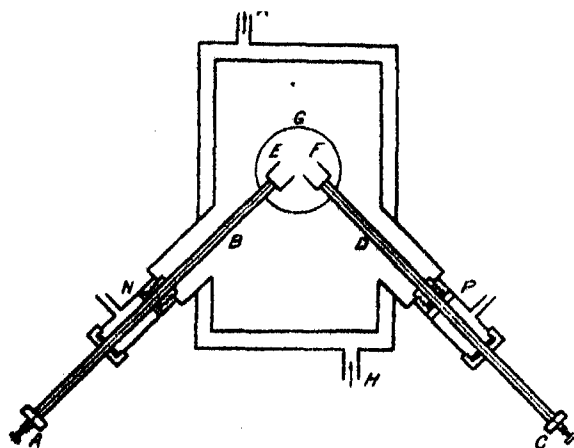
Fig. 1.

It was provided on opposite sides with windows of fused quartz, one of which is shown at G. The electrodes consisted of two steel cups, E and F, connected by wires to the binding poles A and C. These were supported by, but insulated from, two brass tubes B and D which in turn entered the lamp through two oil-sealed, close-fitting stuffing boxes. Preparatory to operating the arc, the cups E and F were filled with metallic lithium, and the chamber was highly exhausted with a set of Gaede rotary oil and mercury pumps. While the arc was in operation the pumps were kept running in order to clear away any gas given out by the electrodes. The arc was

started by bringing the two cups, E and F, into contact and then separating them. This vapourised the lithium and it was found that with currents of from 10 to 15 amps. from the 110 volt D.C. mains, strong steady arcs could easily be maintained in the vapour.

The échelon grating, the optical constants for which have been given in a previous paper,[*] consisted of 30 plates 1·004 cm. in thickness, with a width of step of 1 mm.

The data for the glass Lummer plate used are as follows :

		Refractive indices.	
$d = 0.448$ cm.		6563·045 A.	1·50746
$\lambda = 6707.846 \times 10^{-8}$ cm.		5896·155 A.⎫	1·50990
$\mu = 1.50703$		5890·186 A.⎭	
$\partial\mu/\partial\lambda = -288.6$		4861·49 A.	1·51560
$\Delta\lambda m = 0.4364 \times 10^{-8}$		4308·08 A.	1·52025

Dispersion formulæ used—

$$\mu = 1.491324 + \frac{82.2922}{\lambda - 1463.17}$$

and

$$\mu = 1.494199 + \frac{59.3239}{\lambda - 2089.47}.$$

III. *Observations.*

On several occasions during the investigation the spectrum of the radiation issuing from the arc was photographed with a quartz spectrograph. The spectrum obtained is shown in " b " (Plate 4, fig. 2). It consisted of the wave-lengths $\lambda = 6707.846$ A., $\lambda = 6103.377$ A., $\lambda = 4602.37$ A., $\lambda = 4132.44$ A. and $\lambda = 3232.77$ A.

In order to isolate the light of the red line, a Wratten filter, No. 70, was used. From the reproduction shown in (a), fig. 2, it will be seen that the filter sufficed to cut off all light issuing from the arc other than that of the red line.

The diffraction pattern of the red line as analysed by our Lummer plates is shown in Plate 4, fig. 3. It consists of the doublet ordinarily observed with members at a and b, and a third member at c, *i.e.*, in so far as resolution by the Lummer plate revealed its structure the red line consisted of a triplet.

When, however, the line was resolved by the échelon, crossed with a Lummer plate, observation showed it to consist of a quartet. The reason the Lummer plate did not reveal the quartet structure was due to the fact that

* McLennan, 'Roy. Soc. Proc.,' A, vol. 87, p. 269 (1912).
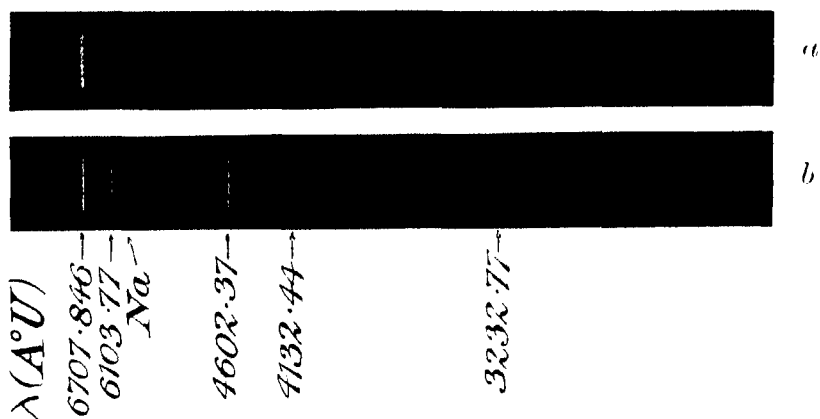
FIG. 2.
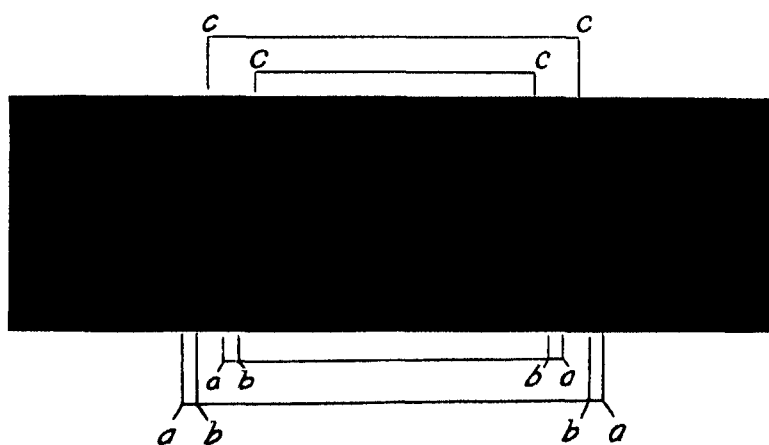
FIG. 3.
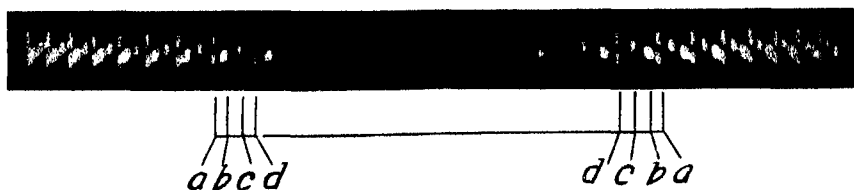
FIG. 4.

the member of shortest wave-length of the quartet of one order overlapped or lay close to the member of longest wave-length of the quartet in the next lower order of the diffraction pattern.

An enlarged reproduction of the pattern obtained with the échelon crossed with the Lummer plate is shown in Plate 4, fig. 4. In it the members *a* and *b* constitute the doublet of the red line as ordinarily observed, and *c* and *d* constitute the new doublet revealed by this investigation.

From measurements made on several plates, the separation between the members *a* and *b* was found by the formula $\Delta\lambda = [\delta(\alpha^2)/\Omega_1]\Delta\lambda_m$* to be 0·128 A.; that between the members *a* and *c* 0·301 A. and that between the members *c* and *d* 0·165 A.

IV. *Discussion of Results.*

(a) *Isotope Doublets.*—In the recent discussion† on isotopes at the Royal Society, Merton, commenting on the fact that the line 6708 A. emitted by lithium, consisted of two components, approximately 0·151 A. apart, stated that if lithium is accepted as a mixture of two isotopes of atomic weights 6 and 7, calculations based on Bohr's theory showed that each of the components of the doublet should be accompanied by a satellite some sixteen times as faint and displaced by 0·087 A. He also stated that he had sought for these satelites but had not been able to observe them. In view of the observation by us of a new doublet accompanying the ordinary doublet of λ = 6708 A., the question of its origin being associated with the isotope of lithium naturally arises.

It is known that with magnetic fields of moderate intensity the sodium line D_1 is resolved into a quartet and the D_2 line into a sextette. As stated above Kent found that the members of the doublet λ = 6708 A. (as ordinarily observed) showed magnetic resolutions in weak fields of the same types as the D_1 and D_2 lines. If, then, we ascribe the two doublets found in our investigations to the isotopes Li^6 and Li^7, our observations would go to show that the members *a* and *b* noted on our plates originated in the same isotope of lithium. If we ascribe the newly observed doublet with members *c* and *d* to the second isotope of lithium, it will be noted that since it appears on the short wave-length side of the doublet *a, b*, it would follow from Bohr's theory that the doublet *a, b*, should be ascribed to Li^6 and the doublet *c, d*, to Li^7, *i.e.*, the radiations from Li^7 should be of shorter wave-length than corresponding ones from Li^6.

(b) *Separations of Doublets.*—On this view it will be seen that from our

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* McLennan and McLeod, 'Roy. Soc. Proc.,' A, vol. 90, p. 246 (1914).

† 'Roy. Soc. Proc.,' A, vol. 99, p. 87 (1921).

measurements the separation of the Li^6 doublet is 0·128 A. and that of the Li^7 doublet 0·165 A.

Observations on corresponding series lines in the spectra of Na, K, Rb and Cs have made it clear that the doublet frequency differences with these elements are directly proportional to the squares of the atomic weights. If this law be applicable to lithium it would follow that wave-length differences for the two doublets of Li^6 and Li^7 at $\lambda = 6708$ A. should be approximately 0·55 A., which it will be seen is between three and four times the doublet separations observed in our experiments. The values obtained by us, however, for the separations of the two doublets are of interest in connection with this law, for according to it the separations for the Li^7 and Li^6 doublets should be in the ratio 49/36, *i.e.*, 1·36 : 1·00. As the ratio of the separations found by us was 1·30 it will be seen there is fair agreement.

(c) *Displacement of Isotope Doublets.*—It will be noted that from our measurements the average displacement of the Li^7 doublet c and d was about 0·32 A. on the shorter wave-length side of the Li^6 doublet a and b. This displacement is, therefore, between three and four times as great as the calculated separation given by Merton, namely, 0·087 A.

(d) *Isotope Displacement and Atomic Number.*—In 1917, Aronberg[*] in studying the line $\lambda = 4058$ A., emitted by a specimen of radio-lead of atomic weight 206·3318, observed a difference of 0·0044 A. between the wave-length emitted by this specimen and that emitted by ordinary lead of atomic weight 207·29. This result was also confirmed by Merton,[†] who found a difference of wave-length for radio-lead from pitchblende and ordinary lead of 0·0050 ± 0·0007 for the same wave-length. As the difference in wave-length one would expect to obtain in this case on the Bohr theory for the line $\lambda = 4058$ is 0·00005 A., it will be seen that the observed wave-length difference was between eighty and ninety times as great as the calculated amount.

Taking this result in conjunction with our own observations on lithium, it would appear that with lead and lithium the observed isotope displacements can be very closely obtained by multiplying the displacements calculable on the Bohr theory by the atomic numbers of the respective elements.

If it should turn out that such a law were applicable generally to isotopic displacements, it would bring the spectral isotopic displacements of a number of the elements easily within the scope of observation open to us, with high

* 'Aronberg, 'Proc. Nat. Acad. Sc.,' vol. 3, p. 710 (1917); 'Astrophys. Jour.,' vol. 47, p. 96 (1918).

† Merton, 'Roy. Soc. Proc.,' A, vol. 96, p. 388 (1 20).

resolution ruled gratings and with échelon gratings and Lummer plates of the resolving powers already developed.

(e) *Intensity of Doublet Components.*—During the course of the experiments visual comparisons were frequently made of the relative intensities of the members of the quartet. It was noted that irregular fluctuations in these relative intensities always accompanied variations in the strength of the current in the arc. When the arc was steady and at its brightest, the members *b* and *d* appeared with the greatest relative intensity, *i.e.*, the shorter wave-length member of both the Li^6 doublet and of the Li^7 doublet, appeared to be of stronger intensity than the longer wave-length members of these doublets. Of all four members of the quartet the component " *b* " (the shorter wave-length member of the Li^6 doublet) always possessed the greatest intensity. This result for each of the doublets is in keeping with observations made on the relative intensities of the D_1 and D_2 lines, in the spectrum of sodium. Voss,[*] who has made a careful investigation of this point, found D_2 to be always the more intense of the D lines, with a maximum value for the ratio of the intensities $D_2/D_1 = 2$ correct to within 10 per cent.

(f) *Identity of Components.*—As the chemically determined atomic weight of lithium is 6·94, it would appear that in ordinary samples of lithium there should be present about sixteen times as much of the Li^7 type as of the Li^6 form. With this in mind one might expect the lines of Li^7 to be of greater intensity than those of Li^6. This would mean, on the view of the identity of the components taken above, that the members *c* and *d* should be of stronger intensity and be more persistent with low arc currents than the members *a* and *b*. The results of our observations, however, were directly opposed to this conclusion.

Another view to take of the identity of the components of the quartet would be to ascribe the components *a* and *c* to Li^6 and the components *b* and *d* to Li^7. This would make our observations on the relative intensities of the components fit in with the relative amounts of Li^6 and Li^7 present in lithium, as determined by the chemically measured atomic weight of the element. On this basis the doublet separation for Li^6 would be 0·301 A., and that for Li^7 0·338 A., values that are nearer to the value 0·55 A. calculated on the basis of the law known to hold for the other alkali elements. The isotopic separation on this view would be between 0·128 A and 0·165 A.

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[*] Voss, ' Phys. Rev.,' vol. 11, No. 1, p. 21 (January, 1918).

V. *Observations on other Wave-lengths.*

A cursory examination was made of the structure of other lines in the spectrum of lithium, and it was found that the wave-length $\lambda = 6103 \cdot 77$ A. consisted of at least three well defined components. It was found difficult to make accurate visual observations as regards the wave-length $\lambda = 4602 \cdot 37$ A., but it was definitely seen to be resolved and consequently it had as a minimum two components. Detailed results of the measurements being made on these wave-lengths will appear in a later communication.

We desire to express our indebtedness to Mr. J. F. T. Young for calculations on the dispersion of the Lummer plate used in the experiments, and to Miss Cale and Mr. P. Blackman for assistance in preparing the illustrations in this paper.

Interfacial Tension and Hydrogen-Ion Concentration.

By H. HARTRIDGE and R. A. PETERS.

CONTENTS.

Section 1.—INTRODUCTION.

The predominance of hydrogen-ion concentration (1) in the colloidal chemistry of the proteins and other substances (Loeb (2)) makes imperative an investigation of those changes at the interface between two phases which are brought about by changes in hydrogen-ion concentration. Previous investigators have directed their attentions to the purely chemical aspects of the interfacial tension between soap solutions and oils, or to non-reactive chemical substances, such as benzene. Using a drop-weight method of measuring interfacial tension, Donnan (3) showed that crude rape oil and crude olive

oil showed a much smaller interfacial tension against alkaline solutions (NaOH and Na carbonate) than against distilled water. The same olive oil showed no such difference against N/1000 NaOH after a process of purification, which was intended to remove the fatty acid. He also found that a paraffin showed no difference for interfacial tension when N/100 NaOH was substituted for distilled water, whereas the same paraffin containing 0·6 per cent. stearic acid, showed a large decrease when in contact with the alkaline solution. The decrease in interfacial tension, so produced, was found to be a function both of the amount of fatty acid dissolved in the paraffin, and also of the amount of alkali. It was further shown that of the series of acids, formic, acetic, butyric, caprylic, lauric, and stearic, tried respectively in solution in the paraffin, stearic and lauric acids alone showed any appreciable lowering of surface tension when an alkaline aqueous fluid was substituted for distilled water.

Harkins and Humphrey (4) extended Donnan's work by showing that alkali (NH$_4$OH) lowered the interfacial tension of benzene solutions of butyric and acetic acid against water. The depression of interfacial tension so produced was a function of the concentration of fatty acid, but tended to become maximal for butyric acid at a concentration of 0·5 mols. per litre. Later, Clowes (5) showed that the decrease in interfacial tension produced by alkalis, such as Na, K, Li, at the interface crude olive oil-water, was lessened by the presence of divalent salts, such as Ca and Ba.

Methods and Technique.

Early in this research we used a capillary height method. For this was substituted a more reliable drop-weight technique. Some measurements were also made by a ripple method.

Drop-weight Method.—A 1 c.c. graduated pipette was turned round at the lower end. The turned-up end was ground as flat as possible. (In some experiments a pipette has been used with turned-down tip, *i.e.*, the aqueous phase has been dropped into the oil.) It was then attached to a small piston, fitted with a screw at its upper end. By turning the screw it was thus possible to fill the pipette with the liquid to be tested, and also to control very accurately the quantity of liquid delivered during the formation of single drops.

All apparatus used in connection with the work was carefully cleaned using for the most part boiling *aqua regia*, with a preliminary treatment with alcoholic potash if necessary.

The buffer solutions used (namely, phthalate, phosphate, and borate) were 0·05 M concentration of these constituents, as described by Clark and Lubs (6).

The hydrogen-ion concentration required in a given case is obtained by adding soda. The term " buffer " is here used in the physiological sense to denote a fluid in which the hydrogen-ion concentration has been stabilised by the addition of the salt of a weak acid.

The buffer solutions were put into glass weighing bottles of convenient size which were then placed side by side in a beaker of water, which acted as a convenient water bath. Some of the liquid under investigation was poured upon the top of the acid buffer. The pipette was lowered into the liquid to be investigated, and some of the fluid drawn up into it as far as the zero mark. The pipette was then lowered, so that its nozzle was completely immersed in the buffer solution, and a small amount of buffer solution drawn into the end of it so as to wet the tip. This was a necessary precaution, since the drops should come from the inner edge of the tip and not the outer, as the liquids used did not wet the glass.

The readings given for the drop volume are the average of several determinations. Care has been made to render the readings as far as possible comparative. In all cases the drop was finally allowed to break away slowly. As has been pointed out by many observers, the drop values for the most viscid fluids, like triolein, require a considerable time for attainment of equilibrium. The average error in the reading of the pipette was approximately 0·002 c.c. Where 0·5 c.c. of fluid has been run out, the total error upon the reading might amount to 1 per cent. The average of three readings should reduce the error considerably.

The values for the interfacial tension have been calculated, using as a basis the values for the interfacial tension of water-benzene, which have been found by careful measurement by Harkins and Humphrey (4) to be 34·98 dynes at 10° C. and 34·52 dynes at 20° C.* Equation (1) was used for calculating the interfacial tension T_{AB}.

(See Hardy)
$$T_{AB} = \frac{b (D_B - D_A) g}{nrf}.$$
(1)

Here, b = volume of drop in cubic centimetre,

D_B = density of aqueous layer,

D_A = density of benzene,

g = gravity (981),

r = radius of tube,

f is an empirical factor,

n = number of drops (taken as 1).

* We are aware that the use of benzene for calibration is open to criticism, but do not consider that it affects the comparative accuracy of our results. Two different bore pipettes calibrated in the above manner gave almost identical results.

rf was found by direct determination of the drop volume for the benzene water interfaces for this apparatus. Table I shows the calculation of the constant.

Table I.

Temperature.	Volume, 1 drop.	D$_B$.	D$_A$.	T$_{AB}$.	*rf.*
9·7° C.	0·06365	0·9998	0·8918	34·99	19·24
20·7° C.	0·05717	0·9981	0·8781	34·49	19·51

Interpolated values of *rf* have been used in calculating the results.

Some of our observations have also been confirmed by the ripple method, first applied practically by Rayleigh (7). This is fully described later.

Temperature.

Experiments have been made at room temperature, and the interfacial tensions have been calculated for the temperature of the experiment without attempt to reduce to a common standard. Temperature variations in interfacial tension have been shown to be small.

Purification of Olive Oil.

Two empirical methods have been used for the purification of olive oil in these experiments. (1) The crude olive oil has been boiled for 12 to 36 hours with frequent changes of tap water and then allowed to cool. (2) The oil has been purified by fractional crystallisation at −5° C.

Section 2.—THE RELATIONSHIP BETWEEN HYDROGEN-ION CONCENTRATION AND INTERFACIAL TENSION.

Measurements of the interfacial tension between purified olive oil and aqueous fluids of various P$_H$* performed with the drop-weight method showed that there is a gradual fall in drop weight as the aqueous phase becomes more alkaline.

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* The "Sørensen" notation is used throughout to express hydrogen-ion concentration (C$_H$):—

$$pH = -\log C_H, \textit{i.e.}, \text{if } C_H = 10^{-2}, \; pH = 2.$$

Table II.—Aqueous Phase dropped into Oil.

P.H.	Buffered fluid.	Drop volume.	Interfacial tension in dynes per cm.
3·0	Phosphate	0·117	14·7
4·0	Phosphate	0·117	14·7
4·4	Phthalate	0·118	14·8
5·0	Phosphate	0·112	14·1
5·6	Phosphate	0·092	12·5
6·0	Phosphate	0·088	11·9
6·4	Phosphate	0·082	10·7
6·4	Borate	0·082	10·9
7·0	Phosphate	0·072	9·6
7·0	Borate	0·076	10·1
7·6	Phosphate	0·059	7·7
7·6	Borate	0·058	7·7
8·0	Phosphate	0·047	6·1
8·0	Borate	0·045	5·9
8·6	Phosphate	0·027	3·4
8·6	Borate	0·026	3·4
9·2	Borate	(Unmeasurable)	(Unmeasurable)

A similar result is also obtained if the capillary height method of measurement be employed.

Table III.

P_H.	Capillary height in mm.		Interfacial tension in dynes per cm.
	Tube (a).	Tube (b).	
4·0	51	—	13·5
5·0	49	—	13·0
6·0	46	—	12·2
6·6	—	31	11·7
6·8	—	29	11·0
7·0	37	26	(9·8)
7·2	—	24	9·1
7·4	—	23	8·7
7·6	—	22	8·3
8·0	28	—	7·4
9·0	0	—	2·4

And the two different methods of measurement give confirmatory results as shown in fig. 1.

It was not conclusively shown, however, that the change in drop weight and capillary height was actually produced by a change in the interfacial tension since in both methods the glass forms a third phase which may introduce effects due to angle of contact.

A method was, therefore, developed which was not liable to such effects, viz., the ripple method, first applied practically by Rayleigh (7). This

observer measured by its means the surface tension of water under various conditions. Dorsey (8) improved the technique and determined the surface tension of various aqueous solutions. Watson (9) has used the method for determining the interfacial tension of various organic liquids against mercury. The principal difficulty met with is connected with the measurement of the waves, because when the two liquids are of nearly the same refractive index the intensity of the light reflected from the interface is
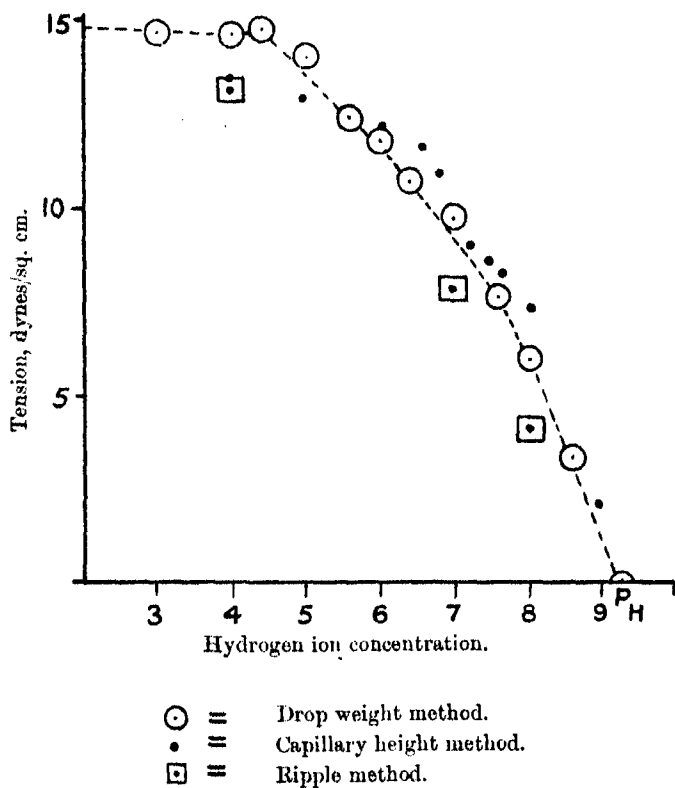
Fig. 1.

small. For this and other reasons the method was reconsidered, and the following alterations in the design of the apparatus were effected.

(1) The transmitted beam is measured in preference to the reflected beam.

The three observers mentioned above made their measurements in the light reflected from the top surface of fluid or mercury as the case might be.

(2) In the original apparatus two synchronous electrically-driven tuning-forks were used, one for creating the waves and the other for rendering the beam of light intermittent. These were replaced by a motor-driven shaft,

which operated a system of levers for setting up the waves and also a rotating sector for rendering the light intermittent. The diagram (fig. 2) below gives a general view of the apparatus.

The beam of light, having passed through the condenser and interrupter,
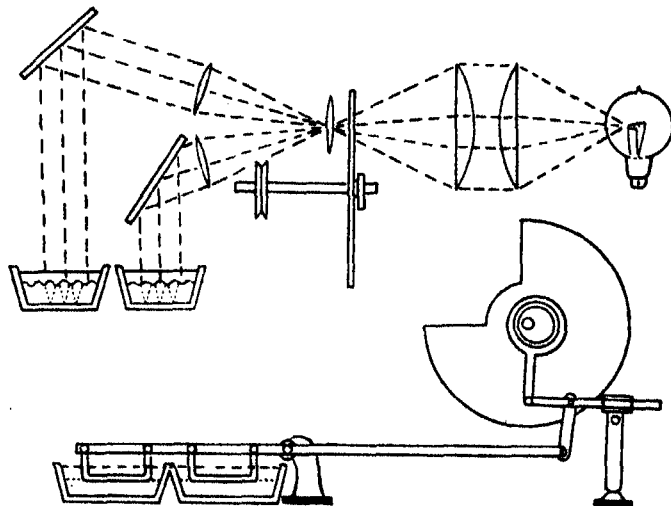
Fig. 2.

was rendered parallel by the collimators, and was then directed down on the surface of the liquids by means of the mirrors. These beams were refracted at the interface between the liquids by the waves, which act like weak cylindrical lenses, so that lines of light are formed on the bottom of the trough. Each of these lines corresponded to the crest of one of the waves, and, therefore, by measuring the distance between the lines by a suitable milli-metre scale the wave-length of the ripples at the interface is ascertained.

Preliminary experiments with this apparatus showed that while ripples are propagated a considerable distance when benzene forms the upper phase, even strong waves are propagated only a very short distance when pure olein forms the upper liquid. This is presumably due to the considerable viscosity of this oil.

A mixture of equal parts of olein and benzene was therefore tested with more satisfactory results. Even with this mixture, however, it is not possible to observe more than four waves at a time. Further, if the amplitude of vibration of the dipper setting up the ripples was made too great, an emulsion of the oil phase was formed in the aqueous phase. The levers which conveyed motion to the dipper from the eccentric on the motor-driven shaft were, therefore, modified so that the amplitude of vibration of the dipper could be adjusted while the apparatus was in action, the greatest

amplitude being employed that did not cause emulsification. The apparatus which ran off 100-volt direct current produced approximately 2500 vibrations per minute, but the number of vibrations was not sufficiently steady to form the basis of reliable measurements. Two alternatives presented themselves : (1) to use an alternating current and a synchronous electric motor (2) to set up oscillations in two troughs side by side, and keeping one constant, to vary the conditions to be investigated in the other. The latter alternative was tried with satisfactory results and the following values obtained :—

Table IV.—Interfacial Tension by Ripple Method of 50 per cent. Olein in Benzene against Phosphate Buffered Solutions.

P_H.	Vibrations per second.	λ in cm.	ρ density of oil above.	ρ' density of aqueous phosphate.	Tension in dynes per sq. cm.
4·0	41·4	0·295	0·90020	1·0808	13·4
7·0	41·4	0·248	0·90020	1·0598	8·0
8·0	41·4	0·200	0·90020	1·0458	4·2

The values in the last column were calculated from the data given in the Table according to the following formula :—

$$\text{Tension in dynes per sq. cm.} = \frac{\lambda^3 (\text{vibs. per sec.})^2 (\rho + \rho')}{(2\pi)} - \frac{\lambda^2 g (\rho' - \rho)}{(2\pi)^2}. \quad (2)$$

This formula is modified from one given by Lamb (10) and incorrectly quoted by Dorsey (8).

It will be observed that the values obtained by the ripple method are somewhat lower than those given by the drop-weight method, but it seemed to us to be outside the scope of this research to seek the cause of this difference, since the values that we obtained showed the same fall in the interfacial tension between the oil and the aqueous solution as the latter became more alkaline, that the capillary height and drop-weight methods had demonstrated. It was therefore clear that a true change in interfacial tension had been brought about and not merely a change in the so-called angle of contact.

Conclusion.

Measurements of interfacial tension by the capillary-height, drop-weight and ripple methods of measuring interfacial tension agree in showing a decrease in interfacial tension between olive oil and various aqueous buffered solutions as the aqueous phase becomes more alkaline. This decrease is, at any rate in large measure, determined by the C_H of the aqueous phase. In

the remainder of the paper these conclusions are amplified, using the drop-weight method, which has been shown to be valid in this connection.

Section 3.—Effect of Concentration of Glyceride (or Fatty Acid) and Alkali on the Interfacial Tension.

One of Donnan's outstanding results was that when an alkaline solution is substituted for distilled water in contact with fatty acid dissolved in benzene or petroleum, or even when associated with triglyceride, a decrease in interfacial tension is produced which is found to be a function both of the concentration of fatty substance and of the amount of alkali present.

We repeated these experiments with buffered solutions and in most respects amply proved Donnan's conclusion. For example, in the following Tables (V and VI) are given the interfacial tensions of various fatty acids and oils in benzene against acid and alkaline phosphate buffered solutions, and in two cases the effect of varying the concentration of the fatty substance in benzene is shown.

Table V.—Fatty Substances dropped through Aqueous Phase.

Substances in benzene.	Concentration grammes of substance in 100 grm. of benzene.	Temperature.	Concentration of buffer.	Interfacial tension in dynes per cm., against	
				Acid phosphate buffer P_H 5·6.	Alkaline phosphate buffer P_H 7·6.
		° C.			
Lauric acid*	0·71	22·0	Full	29·8	23·1
Palmitic acid*	0·098	7·8	,,	33·3	27·8
,, ,, *	0·098	15·1	$\frac{1}{3}$	31·9	28·7
,, ,, *	0·098	28·0	$\frac{1}{3}$	32·4	28·4
Behenic acid*	0·336	28·0	Full	33·1	26·2
Oleic acid	0·98	16·2	,,	25·4	16·2
Elaidic acid*	0·091	16·3	$\frac{1}{3}$	31·4	27·7
Ricinoleic acid	0·1 (?)	17·1	$\frac{1}{3}$	21·0	13·8
Palmitic acid	0·152	19·6	Full	—	29·3
,, ,,	0·076	20·0	,,	—	30·7
,, ,,	0·0076	20·5	,,	—	33·6
,, ,,	0·00076	21·0	,,	—	34·4
,, ,,	0·000076	21·3	,,	—	34·8
,, ,,	zero	20·0	,,	—	34·5
Triolein†	0·281	16·1	Full	29·4	27·7
,, †	0·499	16·0	,,	29·2	27·0

* Pure specimens kindly supplied by Mr. N. K. Adam.
† Pure French specimen kindly supplied by Mr. Hardy.

Table VI.—Tripalmitin in benzene, 1·13 per cent. by weight.

Density taken as that of benzene borate and phosphate solutions, full buffer strength.

Aqueous phase.	P_H.	Temperature in °C.	Interfacial tension in dynes per cm.
Distilled water	—	13·5	33·6
Borate	5·0	13·5	31·5
Phosphate	{ 5·6	{ 18·5	{ 30·2
	{ 5·6	{ 16·1	{ 30·8
	7·4	15·9	29·6
	8·2	18·5	29·8
Borate	9·2	13·5	25·9
	10·0		
NaOH—			
N/1000	11·0	13·5	24·5
N/20	12·7	14·0	17·0

Tripalmitin showed the first significant fall in interfacial tension at a more alkaline *p*H than triolein. We have not studied the reason for this difference from triolein, which may possibly be correlated with its higher melting point.

The above Tables V and VI show in the case of palmitic acid and of triolein in benzene the effect of changing the concentration of the fatty substance on the interfacial tension. They confirm and add to Donnan's results with stearic acid in paraffin, and to those of Harkins and Humphrey (4) for butyric acid in benzene. It will be noted, however, that, contrary to Donnan's conclusions, both triolein and tripalmitin show a lower interfacial tension for the alkaline solution than for the acid one. In the case of triolein, this is small owing to the small concentration studied.

We will now give in tabular form our results for the effect of concentration of buffered solution upon the interfacial tension.

Broadly speaking Table VII confirms Donnan's conclusions that as the concentration of the alkaline phase decreases there is a rise in interfacial tension; that is, interfacial tension increases when distilled water is replaced by the alkaline fluid. We have now to consider the effect of dilution upon the *p*H of the buffer solution. Experiments showed that in the case of phosphate solutions, dilution to 1/10th of the full strength caused a negligible change in the hydrogen-ion concentration as measured by indicators. With further dilution a change in the *p*H set in. If we confine ourselves to dilutions of alkaline buffer solutions up to 1/10th full strength, we see that oleic acid alone shows a large change in interfacial tension; so does the same acid in benzene. Triolein in benzene, on the other hand, shows some 1 per cent. variation only (within the limits of experimental error). Palmitic acid

showed some 6 per cent. change.   The interfacial tension for triolein therefore appeared to depend upon pH, whereas some other factor seemed to be concerned in the case of oleic acid.

Table VII.—Fatty Substance dropped through Aqueous Phase.

Substance.	Concentration of substance grammes per cent.	Temperature.	Concentration of buffer.	Interfacial tension in dynes per cm., against	
				Acid phosphate buffer original P_H 5·6.	Alkaline phosphate buffer P_H 7·6.
Oleic acid	100	° C. 16·0	Full	12·7	1·4
			0·5	13·7	4·8
			0·4	—	6·3
			0·25	—	8·8
			0·17	——	11·1
			0·1	13·9	12·8
		·	0	12·7	12·7
Palmitic acid in benzene	0·098	18·0 (?) 16·6 18·2 18·7	Full 0·5 0·1 0·01	33·3 — 32·3 —	27·8 27·7 29·1 31·9
Oleic acid in benzene	0·983	16·0 16·0 16·0 16·0	Full 0·5 0·25 0·1	25·4 24·7 24·9 24·5	16·2 16·9 18·2 19·4
Triolein in benzene...	0·409	16·0 16·2 16·0	1·0 0·5 0·1	29·2 28·7 28·7	27·0 27·0 27·4

Table VIII brings out another difference in the behaviour of fatty acids and oils, for whereas the latter show the same interfacial tension for phosphate and borate solutions of the same P_H the fatty acids or solutions of them do not.

This Table not only illustrates the different behaviour of oleic acid and olein to phosphate and borate buffered solutions, but it also shows their differences to weak unbuffered soda solutions.   The situation may be summed up by the statement that whereas the oleic acid interface is "protected" against unbuffered soda solutions, it is at the same time abnormally "exposed" to the decrease in interfacial tension produced by buffered phosphate solutions. An explanation will now be given for these apparently contradictory properties.

Table VIII.—Aqueous Phase dropped into Oil.

Substance.	Concentration (per cent.).	Temperature.	Concentration of buffer.	Interfacial tension in grammes per cm., against		
				Phosphate buffer P_H 7·6.	Borate buffer P_H 7·6.	NaOH N/100.
		° C.				
Olein	100	15	¼	7·4	7·2	Unmeasurable.
Olein in benzene	50	15	¼	7·7	7·7	Unmeasurable.
Oleic acid A......	*100	—	1	1·4	16·4	11·0
Oleic acid B......	†100	—	½	10·8	17·8	
Oleic acid A in benzene	98	20·4	1	16·2	15·4	13·8
Oleic acid B in Olein	20	15	¼	2·9	5·8	5·5

* Oleic acid A was a Kahlbaum's specimen—it was found to be very acid. Water shaken with it was found to be acid to brom-cresol blue (below P_H 4·6 about).

† Oleic acid B was a "pure specimen" kindly supplied by Mr. W. B. Hardy. It was found to be acid to brom-cresol purple (below P_H 5·6 about).

Cause of Discrepancy between Behaviour of Oleic Acid against Borate and Phosphate Buffer Solutions of the same P_H.

During the course of experiments performed to ascertain the cause of the behaviour of oleic acid to phosphate and borate buffer solutions of the same P_H, the observation was made that when oleic acid is in contact with an alkaline fluid, there is a neutralisation of base near the interface such as does not occur if olein is used instead. Thus if a suitable indicator be added to the aqueous liquid, the change in reaction towards acid can be watched taking place near the interface. (In the case of weak ammonia solutions, neutral olein brings about a similar change.) This disappearance of base is also shown by a change in interfacial tension; for if the drop is caused to form and fall rapidly a small drop breaks away, showing a low interfacial tension; if, on the other hand, the drop is caused to form slowly a larger one breaks away, showing that the interfacial tension is now higher owing to the disappearance of base from the interface. Thus N/100 soda gave with neutral olein an immeasurably small drop, demonstrating the low interfacial tension that would be expected for a fluid so strongly alkaline. This same solution gave with oleic acid quite large drops (0·04 c.c.) showing the disappearance of base from the interface and a consequent rise in the hydrogen-ion concentration and interfacial tension. This disappearance of base and conse-

quent production of a high interfacial tension could not have been due to the oleic acid itself. For if base had combined with the oleic acid, soap would have been formed. This, far from raising the interfacial tension, is known to lower it. The effect must, therefore, have been due to other acid substances associated with the oleic acid. Now, all samples of oleic acid tested by us were acid to litmus; it is stated that pure oleic acid should be neutral (11); our samples must, therefore, have contained acid impurities. It is known that quite simple acids, even such as acetic and formic acids, are formed in oleic acid upon standing, owing to absorption of oxygen (this is why samples of oleic acid tend to become rancid). It seems reasonable to conclude that our samples contained such acid impurities of low molecular weight. These would form simple salts readily diffusible into the body of the aqueous phase.

Three pieces of evidence can be advanced in confirmation of this view.

(1) That whereas pure oleic acid should be neutral to litmus paper, all the samples we had used gave a full acid reaction. Further, distilled water shaken with them was found to be acid to brom-cresol purple, i.e., was below P_H 5·6.

(2) That thoroughly washing our oleic acid with water not only made it nearly neutral to litmus, but also caused it to behave more like neutral olein.

(3) That the addition of acetic acid to olein causes it to behave as we had found oleic acid to do.

These statements are supported by the values given in Table IX.

Table IX.—Aqueous Phase dropped into Oil.

	Interfacial tension in dynes per cm. between		Difference in interfacial tension.
	Phosphate buffered solution P_H 7·6.	Borate buffered solution P_H 7·6.	
Neutral olein	7·4	7·2	+ 0·2
Olein† acetic acid 0·1 per cent.	6·7	9·4	− 2·7
Oleic acid in benzene*	6·25	7·5	− 1·25
Oleic acid in benzene†	5·33	5·38	Within experimental error.

* Acid to litmus.
† Nearly neutral to litmus.

The conclusion to be drawn from the above figures is that, if either olive oil or oleic acid, in which foreign acids are present, are brought into contact with buffered aqueous fluids, then if those fluids contain a low concentration

of sodium ions (*e.g.*, borate buffers) a considerable rise in the hydrogen-ion concentration of the aqueous phase will occur at the interface, with a corresponding rise in the interfacial tension. Whereas if those aqueous fluids contain a high concentration of sodium ions (*e.g.*, phosphate buffers) only a slight rise in the H-ion concentration of the aqueous phase will occur at the interface, and therefore the rise in interfacial tension will be only a small one.

This conclusion fits in with the data at our disposal, and fully accounts for the difference in the behaviour of olein and oleic acid to buffered fluids. This explanation also covers the differences in their behaviour to unbuffered alkaline fluids, which are shown in Table X.

Table X.—Aqueous Phase dropped into Oil.

Against.	Purified olein.	Purified olein* 5 per cent. oleic acid.	Purified olein* 20 per cent. oleic acid.	Oleic acid.	Olein* 0·2 per cent. acetic.
Distilled water	19·4	20·3	18·3	22·2	17·9
N/1000 NaOH...........	12·0	11·9	15·7	22·0	17·5
N/100 NaOH	0	0	5·2	11·1	3·2
Specific gravity	0·917	0·910	0·896	0·808	0·916
Reaction to litmus	Neutral	Neutral	Slightly acid	Acid	Acid.

* Approximately.

The effect of the foreign acid in raising the interfacial tension is well seen in the case of N/100 NaOH. Whereas pure olein, or that to which 0·5 per cent. oleic acid had been added, gave an unmeasurably small tension; that containing 20 per cent. oleic acid, or 0·2 per cent. acetic, gave measurable tensions of 5·2 and 3·2 respectively. Further increase in either acid was found to raise the tension still further. We need hardly point out that, according to Donnan, purified olein should show no change of interfacial tension with increase of concentration of alkali, whereas oleic acid should show a large change, *i.e.*, the precise converse to the results shown in the above Table.

The practical conclusion to be drawn from the above experiments is that, when a pure triglyceride such as olein is brought into contact with different buffered fluids of the same P_H, the same interfacial tension is developed. If, however, oleic acid is present, then its liability to go rancid and become acid to litmus renders the interfacial tension values unreliable.

Behaviour of Purified Olive Oil against N/1000 NaOH.

With regard to the discrepancy between our results and those of Donnan for the interfacial tension of purified olive oil against N/1000 soda, which led him to the view that oils only interact with bases to cause a fall in interfacial tension when they contain fatty acids as an impurity, we must admit the failure of all our attempts to prepare an oil which did not give a fall in interfacial tension when N/1000 NaOH was substituted for distilled water. Thus, a washed sample of pure olive oil gave a 50 per cent. decrease, and was found by titration to contain 3 per cent. oleic acid. The chemically equivalent amount of baryta was added and the neutral oil again tested; this also gave a 50 per cent. decrease in interfacial tension when N/1000 NaOH was substituted for distilled water. Lastly, this neutral oil was neutralised to phenol red with baryta in dilute alcohol, and removed by extraction with ether. On titration, this sample showed acids to be practically quite absent. Yet substantially the same decrease of 50 per cent. was found in the interfacial tension. We cannot, therefore, explain the discrepancy between our results and Donnan's, although we spared no pains in order to do so. It would seem, therefore, that some other explanation must be advanced for Donnan's result than the one that he gives. We have discovered incidentally that our specimens of olive oil behave in a similar way to Donnan's purified specimens when they have been saturated with CO_2 gas.

Summary of Section 3.

From the results of this section, we conclude that the decrease in interfacial tension between fatty substances in benzene solution and aqueous buffer solutions, depends in part upon: (*a*) the concentrations of fatty substance; (*b*) the hydrogen-ion concentration of the aqueous phase.

An apparent exception to this was found in the case of oleic acid, which showed a greater decrease of interfacial tension against a phosphate buffer solution than against a borate buffer solution of the same *p*H. Evidence is brought forward in support of the view that this was caused by the presence of acid impurities in the oleic acid.

Donnan's results for the interfacial tension of purified olive oil against N/1000 soda could not be confirmed.

In the next section, consideration is given to the question of whether other chemical groups than those studied show interfacial tension differences dependent upon hydrogen-ion concentration.

Section 4.—RELATION BETWEEN CHEMICAL CONSTITUTION AND CHANGE OF
  INTERFACIAL TENSION UPON PASSING FROM AN ACID TO AN ALKALINE
  BUFFERED SOLUTION.

Table XI gives the interfacial tensions (and the densities used in the
calculation) of a number of pure substances against acid and alkaline buffered
phosphate solutions. Care has been taken to make the readings as comparable
as possible.

Table XI.—Substance dropped through Aqueous Phase.

Substances.*	Concentration of buffer.	Density.	Temperature.	Interfacial tension in dynes per sq. cm., against an	
				Acid buffered phosphate solution P_H 5·6.	Alkaline buffered phosphate solution P_H 7·4.
			° C.		
(1) Benzene	1	0·8787	20·2	33·4	33·4
(2) Toluene	1	0·8680	18·2	34·3	34·4
(3) Octane	1	0·7060	17·5	44·6	43·7
(4) Octylene	½	0·7226	16·7	23·1	23·9
(5) Caprylic acid	¼	0·9118	17·0	7·31	6·54
(6) Octyl alcohol	1	0·8290	16·3	8·09	8·76
(7) Hexane	⅕	0·6601	18·0	50·97	49·33
(8) Cyclohexane	¼	0·779	16·3	44·75	45·74
(9) Cyclohexanol	½	0·946	18·0	3·81	3·85
(10) Oleic acid	1	0·898	16·1	12·6	1·45
(11) Ricinoleic	¼	0·9538	17·0	6·85	4·41
(12) Triolein	—	0·915	16·3	20·4	12·1

Note.—The same tip was used throughout the experiments of Tables V, VI, VII, XI.
  * Pure specimens supplied by Mr. Hardy.

Interfacial tension is seen to depend upon two factors: firstly, chemical
constitution, this factor causes the difference between the interfacial tension
of such bodies as octane (45), and octyl alcohol (8), previously described by
Hardy (12); secondly, in certain cases only, upon the reaction of the aqueous
phase.

Harkins, Davies, and Clark (13) have shown that the interfacial tension
between purified benzene, or toluene and water, is not affected by the reaction
of the latter. Table XI shows this to be true (between the limits of pH
investigated) of all the substances tried, with the exception of fatty acids and
triolein; we have previously shown that tripalmitin in benzene solution
behaves similarly. The only substances, therefore, showing change of inter-
facial tension with change of pH, are those which contain the chemically
reactive ionisable group —COOH, free or in combination with glycerine.

Section 5.—EXPLANATION OF THE FALL IN INTERFACIAL TENSION BETWEEN
OILS AND ALKALINE AQUEOUS FLUIDS.

In the preceding sections we have shown that interfacial tension depends
upon pH when a fatty acid, or triglyceride, is present at the interface. This
is clearly not the only factor which can affect interfacial tension. For
instance, Clowes showed, in the paper previously referred to, that the
relative proportion of Na and Ca in the aqueous phase would profoundly
affect interfacial conditions. We have also found that the interfacial tension
of oleic acid against distilled water of varying reaction (produced by traces of
CO_2) does not vary. It therefore appears that a small amount of alkaline
substance is needed to produce the effects studied.

We have come to the conclusion that the following extension of current
views correlates the facts in an orderly manner.

The fall in interfacial tension, which occurs when distilled water in contact
with an oil, or fatty acid, is replaced by an alkaline fluid, is due actually to
the interfacial formation of soap (salt of fatty acids). Further, the amount of
this soap present interfacially, under any given set of circumstances, is
determined by the reaction of the aqueous phase.

The following summarised evidence is in agreement with the view:—

(A) That the condition required for a fall in interfacial tension is that
there must be in the system both a base (such as Na, K, or NH_3) and a fatty
acid or oil.

Phase.	I.T.
Thus 1 Benzene — NaOH	High.
2 Benzene + NH_3 water......................................	,,
3 Benzene — oleic acid in water	,,
4 Olein — water	,,
5 Oleic acid......water	,,
6 Olein...........NaOH solution	Low.
7 Olein...........NH_3 solution	,,
8 Olein...........Na_2CO_3 or borate phosphate, etc.	,,
9 Benzene ......Na oleate...................................	,,
10 Na oleate in olein water......................................	,,
11 Benzene + NH_3......Oleic acid in water	,,

(It should be pointed out that the solution of oleic acid in water was
obtained by dissolving 1 c.c. oleic acid in 1 c.c. alcohol and adding to 8 c.c.
water, and filtering.)

(B) That even when both fatty acid or oil and base are present, the inter-
facial tension remains high if either of the chemically reactive phases cannot

reach the interface owing to the formation of a more stable or less soluble compound elsewhere.

Thus 12 Olein .... Na Cl solution .... I.T. high.

But 13 Olein .... Na Benzoate solution ... I.T. low.

14 Olein .... NH₄OH .... I.T. low.

So also

15 Olein .... NaOH + CaCl₂............ I.T. high.

because calcium oleate is not readily dispersed in water (see Clowes).

Similarly,

16 Lead Oleate in Benzene ... NaOH .... I.T. high.

But remove lead by changing it to the sulphide, and I.T. immediately falls thus—

17 Lead Oleate in Benzene ... NaOH + Na₂S ... I.T. low.

(C) That even if a soap is present and is able to reach the interface, the interfacial tension does not fall if a substance producing elsewhere a more stable or less soluble compound with the soap be present.

Thus 18 Benzene .... Na Oleate solution........ I.T. low.

But 19 Benzene + 2 per cent. HA Na Oleate solution I.T. high.

Similarly,

20 Na Oleate in Olein — HCl .... I.T. high.

The above experiments seem to us to establish the view that the fall in interfacial tension is brought about when both base and fatty acid (or glyceride) are able to interact near the interface. Provided that enough base be present, the reaction of the aqueous phase determines how much soap will be formed in the interface. The interfacial tension is determined by the amount of such soap formed.

Discussion.

(*a*) Though we have confined ourselves to a comparatively narrow range of reaction, it seems clear that hydrogen-ion concentration plays a large part in the type of interfacial change which we have been studying. There seem to be reasonable grounds for thinking that at the interface the —COOH groups of fatty acids are oriented towards the water (Hardy (12), Langmuir (14), Harkins (13), Adam (15)). The effect of P_H is therefore operative upon the oriented —COOH group, an ionisable group, or in Hardy's terms, a group permitting of the "opening up of internal molecular fields." Associated with this, we have the fact (Langmuir and Adam) that a fatty acid occupies a 16 per cent. larger area upon the surface of acid solutions than upon

alkaline ones. A transition from one volume to another occurs abruptly at about $P_H = 5\cdot0$. It is tempting to think that this is in some way associated with the ionisation of the $-COOH$ group. The gradual change in interfacial tension which occurs as the aqueous phase becomes more alkaline quite probably results in a gradual substitution of Na for H in COOH (*i.e.*, the formation of Na oleate at the interface) with a consequent change in interfacial tension. But considerable further experimentation is needed both to prove this and to determine the nature of the gradual change in the structure of the interface as the reaction of the aqueous phase becomes more alkaline. This change in the case of the fatty acid eventually resolves itself into complete aqueous solution as a soap at a P_H of $8\cdot0$ approximately. A correlation of these facts with problems of the iso-electric point of amphoteric and protein-like substances would be of interest.

(*b*) In a consideration of the mechanism by which change in P_H of the aqueous phase produces effects upon the $-COOH$ group at the interface, it is well to remember that Haber and Klemensiewicz (16) showed that, in the case of the benzene-water system, there may be differences of potential of as much as 1 volt produced at the interface by a small change of concentration from base to acid near the neutral point. This electrical change is likely to be an expression of a re-orientation of water molecules at the interface. In the absence of a reactive group it may be that these electrical changes appear instead of changes in interfacial tension.

We feel that the view that we have put forward explains some of the effects observed by Shorter and Ellingworth (17). These observers found that the addition of alkali to soap solutions decreased the observed interfacial tension between these solutions and benzene. This is correlated with the well known effect of alkalies in assisting the emulsifying action of soap solutions. In our view, the effect of the added alkali is due to the decrease in the H-ion concentration of the solution.

One physiological application requires comment. Harkins, Davies, and Clark concluded from their experiments upon the benzene-water interface, that the changes in interfacial tension produced by acid and alkali were not sufficient to account for muscular motion. In criticism, it must be pointed out that, theoretically, all that is needed to obtain the necessary type of interfacial change is a series of $-COOH$ groups arranged so that they can react to changes of hydrogen-ion concentration. Such $-COOH$ groups might well be part of the protein structure of the contractile mechanism of the muscle. Whether changes of a sufficient order of magnitude could be produced would depend largely upon the dimensions and structure of the system.

Summary.

1. A comparison of the capillary height, drop-weight, and a modified ripple method of measuring interfacial tension, shows that the drop-weight method is valid for comparing the interfacial tensions of oils, or fatty acids, against aqueous solutions of varying reactions.

2. Using the drop-weight method the following observations have been made :—

The decrease in interfacial tension between fatty substances in benzene solution and aqueous " buffered " solutions depends upon—

(*a*) The concentration of fatty substance.

(*b*) The presence of a small amount of "available" monovalent alkali in the aqueous phase, *i.e.*, alkali not in combination with strong acid.

(*c*) The hydrogen-ion concentration at the interface.

For a series of pure substances, it is found that the changes in interfacial tension produced by changes in reaction of the aqueous phase (*i.e.*, decrease in interfacial tension with increase of alkalinity) occur only with the substances which have the —COOH group, free or in combination, as glyceride.

A hypothesis is developed to correlate the above conclusions.

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The 27-Day Period (Interval) in Terrestrial Magnetism.

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(Received April 10, 1922.)

§ 1. The so-called 27-day period has been considered by me in several previous papers.* In these there were at my disposal homogeneous results from only a short period of years, while data were wanted from a long period to enable an adequate comparison to be made of magnetic and solar phenomena.

With the aid of a grant from the Government Grant Committee, the daily ranges in the Kew declination curves have now been measured back to 1858, when registration commenced. Use is now made of all the data up to 1900. Owing to the magnetograph being out of action, 1874 had to be omitted, leaving a total of 42 years. Subsequent to 1900 train and tram disturbances introduced some uncertainty. For the present purpose this would not have been serious prior to 1916. Declination ranges had, however, not been measured between 1900 and 1910, and the labour available seemed better devoted to other purposes, in view of the existence of the international "character" figures published at De Bilt from 1906 onwards. For the present investigation these supply ideal material. I have used some of this material before, but data from a number of additional years have since become available, and it seemed desirable to contrast the international data from the 15 years 1906–1920 with the 42 years' Kew declination data.

I propose to consider (1) how the phenomena vary from year to year, (2) how they vary with the season of the year. In either case the international data are considered first, as their representative character cannot be questioned. They are based on independent estimates of disturbance, made at a number of stations in different parts of the world. Comparatively few of the stations, it is true, are in the southern hemisphere, but it has been found that, even in the Antarctic, days of much and little disturbance accord wonderfully well with the international figures.†

The international scheme consists in each station allotting to each day a "character" figure (0 = quiet, 1 = moderately disturbed, 2 = highly disturbed). The international "character" is the mean of the figures allotted. It is given to the nearest 0·1, so that 0·0 and 2·0 represent the extremes.

* 'Phil. Trans.,' A, vol. 212, p. 75, and vol. 213, p. 245 ; 'Proc. Physical Society of London,' vol. 27, p. 198 ; 'Journ. Inst. Electrical Engineers,' vol. 54, p. 419 ; 'Trans. Inst. Mining Engineers,' vol. 55, p. 245.

† "British Antarctic Expedition, 1910–1913" : 'Terrestrial Magnetism,' pp. 134, et seq.

Five days a month have been selected at De Bilt since 1906 as representative quiet days, and of late years five other days have been selected as representative disturbed days. For the earlier years I made the choice of disturbed days myself, selecting in each month the five of largest international "character." In quiet times the international quiet days have mostly characters 0·0, 0·1, and 0·2, but 0·4 or even 0·5 is met with occasionally in disturbed years. The "character" figures 1·9 and 2·0 do occur, but they are very rare. The "characters" of the great majority of the selected disturbed days exceed 1·0, but 0·9 and 0·8, or even 0·7, are occasionally encountered.

The primary object of the international scheme is to discriminate between the days of a single month. If the scale at a particular station were absolutely invariable, the result would be that in very quiet months nearly every day would get a 0, while in very disturbed months 0's would hardly exist. The objections to this lead the observer, consciously or unconsciously, to vary his standard, and whether a particular day is assigned a 1 or a 0 partly depends on whether it occurs in a quiet or a disturbed month. The same cause is operative everywhere, with the result that the mean "character" figure for a month or a year has no exact quantitative significance. The period 1906–20 has included some very quiet and some very disturbed years, yet the mean annual "character" figure has varied only from 0·455 in 1912 to 0·751 in 1918; and three years, 1909, 1915, and 1920, which were certainly not equally disturbed, had the identical figure, 0·620.

The size of the absolute daily range of declination (*i.e.*, westerly extreme—easterly extreme, irrespective of times of occurrence) is not determined solely by the amount of disturbance. Even the range of the diurnal inequality derived from the five quietest days of the month varies much with the season of the year and with sunspot frequency. The maximum generally occurs during the hours when declination is normally above its mean, and the minimum similarly in hours when declination is normally below its mean. Thus the size of the absolute range is partly determined—on quiet days mainly determined—by the amplitude of the regular diurnal variation. Consequently a considerably different degree of disturbance may be associated with the same absolute D range in different months, precisely as happens with the "character" figure.

Consideration of the above phenomena led to the use of the difference from the mean monthly value as the disturbance criterion both for "characters" and ranges.

§ 2. Taking n to denote a representative day—whether quiet or disturbed—in the month, the method adopted for exploring the 27-day period consists in entering in columns headed $n-2$, $n-1$, n, $n+1$, and $n+2$ the values of

the "character" or range for the representative day and the two days immediately preceding and following it. Taking the representative disturbed days, and supposing N of them, we sum the N entries in each of the five columns and take their means. The excesses of these means over the mean from all days represent the "primary pulse" of disturbance. In another series of columns headed $n+25$ to $n+30$ are entered the "characters" or ranges for days from 25 to 30 days later than the representative days. The excesses of the means from the N entries in each of these six columns over the corresponding all-day mean constitute the "secondary pulse."

The representative quiet days (or days of least range) are dealt with exactly in the same way. In their case the primary and secondary pulses show deficiencies below the all-day means.

The pulses associated with the disturbed days (or days of largest range) are described as "positive," those associated with the quiet days (or days of least range) are described as "negative."

For the primary pulse, whether positive or negative, the accepted all-day mean is that for the month or year to which the days in column n belong. For the secondary pulse in the yearly results a mean has been derived from the 12 months commencing with February of the current year. For the secondary pulse in the monthly tables the mean for the following month has been used. For instance, the data for 1906 in Table I represent in columns $n-2$ to $n+2$ the excess over 0·647, the mean for 1906, but in columns $n+25$ to $n+30$ the excess over 0·667, the mean from the 12 months February, 1906, to January, 1907. Similarly, the data for June in Table XII represent in columns $n-2$ to $n+2$ the deficiency from 14·68′, the mean range from all days of the 42 Junes, but in columns $n+25$ to $n+30$ the deficiency from 14·85′, the mean range from all days of the 42 Julys.

The average month contains 30 days, so there is not a full month between, for example, day n and day $n+27$. It did not, however, seem worth while attempting to allow for this. Another objection is that in the case of some months, notably January, there is a rather rapid rise (or fall) of range during the month and the following month. We may expect the selected days of small range to tend to come early, and those of large range to tend to come late in January, with a corresponding difference in the times of occurrence in February of the secondary pulse days. The all-day mean values employed would thus tend to be somewhat too large for the primary and secondary negative pulses, and too small for the primary and secondary positive pulses. The selected January days did, as a matter of fact, show the phenomenon, but not to the extent feared, the mean dates of the selected days of small and large range being respectively 13·1 and 16·5.

Some stations participating in the international scheme have dropped out and new ones have come in, and there have been many changes in personnel. Some stations again have intentionally changed their standard. Thus variations must have occurred in the international standard, quite apart from the psychological cause mentioned above, but the exact nature of these changes would be very difficult to ascertain.

Even the D ranges have experienced a small progressive change of standard. The disturbing force required to produce a given change of D varies directly as H (horizontal force component), and H at Kew increased from 0·175 in 1858 to 0·184 in 1900. Thus a change of 10·0′ in D in 1900 represented fully more disturbance than a change of 10·5′ in 1858.

§ 3. Tables I, II and III give the mean annual results from 1906–20, derived from the international "character" figures. Table I deals with the primary and secondary positive pulses derived from the selected disturbed days (five a month) and associated days. The figures represent excesses over the corresponding all day mean, except in the case of a minus sign, when there was a deficiency. The column headed S/P gives the ratio of the largest excess in the secondary pulse to the amplitude of the primary pulse in column n; the figure for 1908 for instance is derived from 0·210/0·664. The column headed S′/P′ gives the ratio of the largest sum from three adjacent columns in the secondary pulse to the sum of the entries in columns $n - 1$, n, and $n + 1$; in 1908, for instance, the figure is derived from (0·210 + 0·207 + 0·162) ÷ (0·330 + 0·664 + 0·399).

Table II deals in a parallel fashion with the negative pulses, derived from the international quiet days and associated days. When, as usual, no sign is attached, the quiet or associated day's "character" was less than the all day mean value to the amount stated, but when a plus sign is attached it was in excess. The significance of S/P and S′/P′ is the same as in Table I.

Table III gives the difference pulses, primary and secondary, obtained by subtracting the sum of the "characters" for the quiet and associated days from the corresponding sum for the disturbed and associated days, and taking the mean of the differences. A minus sign means that the "character" figure from the representative disturbed or associated day was less than that from the representative quiet or associated day.

The figures in the columns $n - 2$ to $n + 30$ in Table III might have been derived by adding corresponding figures in Tables I and II, but they were derived independently as a check. A difference of one in the last decimal place arises occasionally from purely arithmetical causes. The entries under S/P and S′/P′ in Table III are derived from the pulses in that Table itself.

Table I.—Positive Pulses.   International "Character" Figures.

Year	Sunspot frequency	Primary pulse					Secondary pulse						S/P.	S/P'.
		$n-2$	$n-1$	n	$n+1$	$n+2$	$n+25$	$n+26$	$n+27$	$n+28$	$n+29$	$n+30$		
1906	53·8	0·011	0·278	0·658	0·348	-0·015	-0·045	0·040	0·068	0·026	0·008	-0·040	0·10	0·10
1907	62·0	-0·020	0·297	0·665	0·304	0·067	-0·009	0·061	0·119	0·061	0·051	0·099	0·18	0·19
1908	48·5	-0·001	0·330	0·664	0·399	0·134	0·089	0·210	0·207	0·162	0·015	-0·023	0·32	0·42
1909	43·9	0·037	0·285	0·697	0·365	0·115	-0·095	-0·053	0·127	0·142	0·118	0·082	0·20	0·29
1910	18·6	0·045	0·252	0·584	0·317	0·172	-0·017	0·093	0·183	0·123	0·112	0·055	0·31	0·36
1911	5·7	-0·042	0·269	0·683	0·396	0·146	0·028	0·158	0·346	0·326	0·176	0·063	0·51	0·63
1912	3·6	-0·022	0·257	0·645	0·352	0·050	-0·012	0·166	0·271	0·116	0·045	-0·047	0·42	0·44
1913	1·4	0·132	0·348	0·662	0·368	0·147	0·094	0·234	0·317	0·231	0·146	0·111	0·48	0·57
1914	9·6	-0·005	0·200	0·650	0·318	0·133	0·031	0·016	-0·018	0·032	0·111	0·134	0·21	0·24
1915	47·4	-0·055	0·340	0·742	0·380	0·073	0·161	0·151	0·230	0·183	0·101	0·065	0·31	0·39
1916	55·4	-0·003	0·305	0·707	0·419	0·127	-0·076	-0·017	0·061	0·103	0·076	0·056	0·15	0·17
1917	103·9	-0·021	0·266	0·749	0·351	0·102	-0·024	0·054	0·064	0·077	0·042	0·001	0·10	0·14
1918	80·6	0·069	0·396	0·732	0·372	0·137	0·100	0·167	0·125	0·109	0·079	0·037	0·23	0·27
1919	63·6	-0·091	0·272	0·742	0·441	0·107	-0·030	0·100	0·197	0·212	0·132	0·032	0·29	0·37
1920	38·7	-0·012	0·263	0·712	0·308	0·087	-0·081	0·137	0·264	0·180	-0·008	-0·048	0·37	0·45
Means, all years		0·001	0·291	0·686	0·363	0·106	0·015	0·102	0·171	0·139	0·081	0·039	0·25	0·31
A		-0·011	0·301	0·709	0·363	0·079	0·010	0·086	0·116	0·099	0·064	0·027	0·16	0·22
B		0·016	0·269	0·660	0·359	0·119	0·035	0·143	0·289	0·176	0·119	0·065	0·35	0·43
C		0·024	0·296	0·684	0·355	0·117	0·095	0·183	0·176	0·148	0·119	0·103	0·28	0·34
D		0·003	0·279	0·654	0·366	0·123	-0·002	0·115	0·237	0·174	0·093	0·026	0·35	0·40

Table II.—Negative Pulses. International "Character" Figures.

Year.	Primary pulse.					Secondary pulse.						S/P.	S'/P'.
	n−2.	*n*−1.	*n*.	*n*+1.	*n*+2.	*n*+25.	*n*+26.	*n*+27.	*n*+28.	*n*+29.	*n*+30.		
1906	0·132	0·317	0·502	0·275	0·115	0·087	0·197	0·234	0·130	0·087	+0·061	0·47	0·51
1907	0·131	0·333	0·515	0·240	+0·057	0·059	0·141	0·052	0·051	0·064	0·089	0·27	0·36
1908	0·096	0·305	0·523	0·268	+0·019	0·098	0·198	0·181	0·136	0·086	0·013	0·38	0·47
1909	0·143	0·295	0·518	0·275	0·038	0·005	0·052	0·100	0·112	0·098	0·023	0·23	0·29
1910	0·103	0·351	0·581	0·258	+0·039	0·050	0·177	0·218	0·215	0·045	+0·010	0·38	0·51
1911	0·104	0·277	0·516	0·194	+0·043	0·139	0·256	0·221	0·111	0·043	+0·061	0·50	0·62
1912	0·022	0·190	0·413	0·143	+0·130	0·090	0·052	0·044	+0·083	+0·108	+0·025	0·22	0·25
1913	0·123	0·258	0·433	0·190	0·030	0·126	0·143	0·123	+0·051	0·053	0·004	0·33	0·44
1914	0·073	0·295	0·468	0·160	0·018	0·018	0·058	0·084	0·114	0·079	0·076	0·24	0·30
1915	0·048	0·323	0·550	0·228	+0·020	0·102	0·164	0·225	0·194	0·114	0·102	0·41	0·53
1916	0·100	0·348	0·600	0·216	0·001	+0·049	+0·036	0·139	0·084	0·018	0·058	0·23	0·18
1917	0·083	0·303	0·573	0·246	0·046	0·066	0·164	0·103	0·048	+0·068	+0·046	0·29	0·30
1918	0·158	0·423	0·650	0·334	0·068	0·080	0·085	0·130	0·098	0·005	+0·020	0·20	0·22
1919	0·041	0·299	0·683	0·208	+0·097	0·120	0·038	0·061	+0·022	+0·022	+0·017	0·19	0·19
1920	0·093	0·318	0·537	0·160	+0·133	0·018	0·086	0·198	0·041	0·095	0·015	0·37	0·33
Means, all years													
A	0·097	0·309	0·534	0·226	+0·015	0·066	0·118	0·142	0·088	0·036	0·008	0·27	0·33
B	0·109	0·335	0·575	0·261	0·015	0·081	0·123	0·120	0·059	0·029	0·006	0·21	0·28
C	0·080	0·255	0·457	0·172	+0·031	0·033	0·127	0·118	0·061	+0·005	0·001	0·28	0·33
D	0·082	0·293	0·494	0·193	0·010	0·082	0·122	0·144	0·120	0·082	0·061	0·30	0·40
	0·094	0·284	0·509	0·228	+0·038	0·076	0·147	0·153	0·108	0·016	+0·010	0·30	0·40

Table III.—Difference Pulses.   International "Character" Figures.

| Year. | Primary pulse. | | | | | Secondary pulse. | | | | | | S/P. | S'/P'. |
	n−2.	n−1.	n.	n+1.	n+2.	n+25.	n+26.	n+27.	n+28.	n+29.	n+30.		
1906	0·143	0·595	1·160	0·623	0·100	0·043	0·237	0·302	0·157	0·045	−0·103	0·26	0·29
1907	0·112	0·630	1·180	0·548	0·010	0·050	0·202	0·202	0·112	0·116	0·188	0·17	0·22
1908	0·095	0·635	1·187	0·667	0·115	0·183	0·408	0·388	0·298	0·102	−0·010	0·34	0·44
1909	0·130	0·580	1·210	0·640	0·153	−0·090	−0·002	0·237	0·258	0·217	0·105	0·21	0·29
1910	0·148	0·603	1·165	0·575	0·133	0·033	0·270	0·402	0·338	0·157	0·045	0·35	0·43
1911	0·063	0·547	1·198	0·590	0·103	0·167	0·413	0·567	0·437	0·133	0·012	0·47	0·61
1912	0·000	0·447	1·068	0·495	−0·080	0·078	0·218	0·315	0·093	−0·063	−0·072	0·30	0·31
1913	0·255	0·607	1·096	0·558	0·177	0·230	0·377	0·440	0·282	0·198	0·115	0·40	0·49
1914	0·088	0·495	1·118	0·478	0·153	0·048	0·073	0·087	0·147	0·190	0·210	0·19	0·26
1915	−0·007	0·663	1·292	0·608	0·068	0·263	0·315	0·455	0·377	0·215	0·167	0·35	0·45
1916	0·063	0·653	1·307	0·635	0·128	−0·125	−0·053	0·200	0·187	0·068	−0·002	0·15	0·17
1917	0·227	0·568	1·332	0·597	0·148	0·090	0·218	0·167	0·125	0·110	0·047	0·16	0·21
1918	−0·050	0·818	1·383	0·707	0·205	0·180	0·252	0·255	0·207	0·083	0·017	0·18	0·25
1919	0·063	0·572	1·375	0·648	0·010	0·090	0·138	0·258	0·190	0·110	0·015	0·19	0·23
1920	0·063	0·583	1·248	0·608	−0·047	−0·013	0·283	0·462	0·222	0·087	−0·033	0·37	0·39
Means, all years													
A	0·098	0·600	1·220	0·589	0·091	0·081	0·219	0·314	0·228	0·117	0·047	0·26	0·32
B	0·099	0·637	1·284	0·624	0·095	0·090	0·209	0·237	0·158	0·093	0·033	0·18	0·24
C	0·096	0·624	1·118	0·530	0·088	0·128	0·270	0·347	0·237	0·115	0·066	0·31	0·39
D	0·106	0·588	1·168	0·548	0·127	0·177	0·255	0·321	0·268	0·201	0·164	0·27	0·37
	0·097	0·583	1·104	0·593	0·085	0·074	0·262	0·360	0·282	0·109	0·016	0·38	0·40

The last five lines in Tables I, II and III represent mean values from the whole 15 years, and four groups of years A, B, C, D, representing respectively large area of sunspots, small area of sunspots, high spot latitude and low spot latitude. Particulars are given presently.

A feature in the primary pulses calls first for remark. In Table I a minus sign occurs in 10 years in column $n-2$ and only once in column $n+2$, and the entry in column $n + 1$ exceeds that in column $n - 1$ in all but one year. In Table II, on the other hand, the plus sign occurs in column $n + 2$ in 8 years, without occurring once in column $n - 2$, and the entry in column $n - 1$ is always (numerically) greater than that in column $n + 1$. The positive and negative primary pulses are thus both markedly unsymmetrical.

The C.G. of the primary positive pulse falls in the interval between columns n and $n + 1$, and the C.G. of the primary negative pulse in the interval between columns n and $n - 1$. The exact physical significance of the phenomenon could be arrived at only by dealing with periods shorter than 24 hours, but the general explanation is as follows :

The day immediately following a large disturbance is seldom quiet, while the day preceding it is not infrequently quiet. In fact, one is sometimes tempted to think that a special calm has preceded the storm. Again—in Europe at least—large disturbance is much more common in (Greenwich) night hours than in the day hours, and the most disturbed hours precede midnight. The forenoon hours of a highly disturbed day are often quiet, at least at Kew. For the study of disturbance much could be said in favour of a "day" starting at Greenwich noon. It is a natural if not a certain inference from the phenomena that we may regard the centre of disturbance in the positive pulse as later in time, and the centre of quiet conditions in the negative pulse as earlier in time than noon of the representative day. The difference primary pulse in Table III, on the other hand, is very nearly symmetrical with regard to column n.

We shall first consider only the results for all years combined in Tables I, II and III. Each Table shows a conspicuous secondary pulse, the entry in column $n + 27$ being decidedly the largest. The C.G. of the secondary pulse in Table I comes very sensibly on the up side of $n + 27$ (*i.e.,* between columns $n + 27$ and $n + 28$); while in Table II it comes on the down side. In Table III it is slightly on the up side. The interval between the C.G.s of the primary and secondary pulses seems the same or very nearly the same in the three cases, and seems to slightly exceed 27 days.

Absolutely considered, the amplitude of the secondary negative pulse is less than that of the secondary positive pulse, but relative to the amplitude

of the primary pulse it is at least as large. The similarity of the values of S/P and of S'/P' in Tables I and II seems hardly compatible with the suggestion which has been made that the 27-day period apparent in the quiet and associated days merely represents the fact that since highly disturbed days tend to be 27-day followers of highly disturbed days, all days other than disturbed days must have less than their fair share of such followers. Further evidence of the inadequacy of this explanation has been obtained by examining into the actual sequence of q and d (quiet and disturbed) days from 1906 to 1920. Omitting January, 1906, as no data were available for the previous month, we have a total of 895 selected days of either type. The q and d days each number practically a sixth of the total number of days. Thus the 27-day precursor of 895 average days should be a d day in 149 cases, and a q day in 149 cases. The totals actually observed were: d preceding d 257 cases, q preceding q 234 cases, d preceding q 98 cases and q preceding d 85 cases. If it were a matter of pure chance, the four sequences just specified should each occur ten times in 12 months. The d after d and q after q sequences exceeded expectation, the former in 14 the latter in 12 years. Only 1 year in either case gave a frequency less than ten. The d after q and q after d sequences fell short of expectation, the former in 14 the latter in 13 years, only 1 year in either case giving a frequency greater than ten.

In a sense it may be true that the 27-day period in quiet conditions is partly due to the scarcity of disturbed days among the 27-day followers of quiet days; but in the same way, and to approximately the same extent, the 27-day period in disturbed conditions is due to the scarcity of quiet days amongst the 27-day followers of disturbed days.

§ 4. Before discussing Tables I, II and III further, it will economise space to consider the general results derivable from Tables IV to VII, which refer to the Kew D ranges.

Some defects in the material first call for mention. The limits of registration were exceeded in a few days during magnetic storms. In such cases the value answering to the edge of the sheet was accepted, in place of the missing maximum or minimum. This entailed of course an under-estimate of the range. In most cases the under-estimate was probably small, and any effect on the mean ranges on which the Tables depend must have been trifling. On some days of apparently ordinary character there was a serious loss of trace, and a few days' trace was totally lacking. Such days, of course, had to be omitted. In a few cases days that would naturally have been selected disturbed or quiet days were omitted from the selected days because of the loss of trace on days which were 27 or 28 days later. Even a comparatively

TABLE IV.—Positive Pulses.   Kew Declination Ranges.

Year.	Sunspot frequency.	Primary pulse.					Secondary pulse.					
		$n-2.$	$n-1.$	$n.$	$n+1.$	$n+2.$	$n+25.$	$n+26.$	$n+27.$	$n+28.$	$n+29.$	$n+30.$
1858	54·8	-0'10	4'16	13'75	4'51	-0'37	-0'23	1'45	2'46	2'02	0'30	-0'23
1859	93·8	2·50	6·43	16·68	7·73	2·26	-0·32	1·00	2·25	0·38	0·22	0·94
1860	95·7	1·47	6·58	14·68	3·87	0·37	0·72	0·82	0·67	-0·06	-0·72	-0·04
1861	77·2	-0·05	6·53	14·51	5·03	2·20	1·08	8·20	2·28	1·69	0·87	1·04
1862	59·1	-0·24	4·66	15·82	4·59	-0·80	2·39	1·27	1·08	-0·08	-1·11	1·17
1863	44·0	-0·72	2·63	12·58	5·11	1·37	-0·33	1·01	8·38	2·56	1·79	1·06
1864	47·0	1·07	5·78	14·14	5·84	2·04	1·43	8·59	3·85	8·55	8·74	1·75
1865	30·5	0·40	5·72	16·06	6·18	1·59	-0·50	3·16	5·00	6·07	1·63	0·10
1866	16·3	-1·18	3·84	12·73	4·56	0·39	-0·18	0·82	1·16	1·87	2·03	0·20
1867	7·3	1·47	3·27	11·38	5·20	1·73	2·18	8·36	8·82	3·24	8·00	1·75
1868	37·8	-0·02	8·85	12·79	3·30	0·43	0·51	2·12	3·18	2·18	0·16	1·57
1869	73·9	-0·70	5·92	15·68	5·23	0·07	0·26	-0·79	0·94	2·61	0·81	-0·16
1870	139·1	0·10	7·23	15·94	4·83	-0·23	0·95	0·92	0·01	1·89	8·77	2·54
1871	111·2	-0·79	2·77	13·56	3·42	-0·54	-0·36	2·09	-0·26	-0·08	-0·98	-0·10
1872	101·7	-0·26	7·46	16·35	5·69	1·62	-0·22	2·22	1·78	2·69	3·32	0·56
1873	66·3	-1·47	2·94	11·55	2·35	0·51	-0·38	-0·49	-0·12	1·52	1·09	-1·76
1875	17·1	-0·97	1·51	7·95	2·51	0·35	0·40	0·78	0·65	1·85	0·11	-0·76
1876	11·3	-0·85	2·62	8·21	2·41	-0·66	0·24	-0·62	0·81	0·94	0·72	-0·06
1877	12·3	-0·87	2·31	7·74	2·62	0·19	0·04	2·22	1·60	0·90	-0·32	-0·87
1878	8·4	-0·41	2·24	6·18	1·99	-0·20	-0·54	0·35	1·15	0·52	-0·57	-0·09
1879	6·0	0·37	1·35	5·09	1·37	0·44	0·25	0·85	1·43	1·29	0·79	-0·23
1880	32·3	0·71	2·27	8·25	2·57	0·09	0·47	0·90	1·20	1·24	0·16	-0·31
1881	54·3	-0·57	2·52	7·38	1·93	-0·06	0·67	0·40	1·29	0·60	0·70	1·06
1882	59·7	-0·95	5·29	16·55	2·70	-0·16	-1·71	-0·29	0·55	-0·58	-0·50	0·11
1883	63·7	-1·06	3·89	11·52	3·27	1·14	-0·14	-0·11	1·04	0·20	1·57	0·82
1884	63·5	-0·23	8·61	9·14	3·07	-0·90	-1·04	0·19	0·94	0·68	-0·30	0·41
1885	52·2	0·17	2·24	9·56	2·71	0·66	0·12	0·49	1·01	1·37	1·38	0·71
1886	25·4	1·01	4·25	12·12	3·87	1·07	0·08	2·37	4·27	5·00	2·17	1·35
1887	13·1	0·75	3·45	9·13	4·33	1·51	-0·63	1·46	2·88	8·73	2·34	0·95
1888	6·8	-0·02	3·55	9·61	2·70	-0·19	0·00	2·37	3·34	2·24	0·23	-0·85
1889	6·3	-1·03	1·31	7·88	1·91	0·81	-0·41	0·52	3·14	1·92	0·25	-0·70
1890	7·1	0·32	1·73	5·65	1·75	0·21	-0·09	0·69	0·62	0·46	0·76	1·15
1891	35·6	0·64	3·25	9·83	3·74	2·00	-0·10	1·60	1·49	2·70	1·71	0·47
1892	78·0	-1·54	6·30	17·04	5·20	0·60	-1·34	-1·32	1·41	1·29	0·53	-2·08
1893	84·9	-0·15	2·56	8·65	2·88	0·55	-0·12	0·29	0·80	1·61	0·79	0·50
1894	78·0	-0·91	3·74	15·29	5·31	0·91	-1·27	0·02	-0·05	0·60	1·21	2·70
1895	64·0	0·01	2·35	10·14	8·52	1·53	-0·79	0·53	8·11	2·31	2·79	1·70
1896	41·8	0·65	4·15	11·66	5·87	2·66	1·76	2·88	8·60	3·84	2·90	0·55
1897	26·2	-1·37	2·63	9·21	2·24	-0·62	-0·28	1·13	1·61	1·25	-0·32	0·93
1898	26·7	0·18	4·64	10·69	3·53	0·39	0·65	0·73	2·62	2·74	2·74	0·68
1899	12·1	-0·38	2·68	8·56	2·57	0·85	0·51	2·42	2·26	1·41	0·05	-0·15
1900	9·5	-0·22	1·44	5·22	0·66	-0·17	0·31	1·01	0·30	-0·02	-0·10	0·71
Mean		-0·18	3·75	11·34	3·68	0·61	0·10	1·13	1·76	1·72	0·96	0·45

small loss of trace near the normal time of maximum or minimum disqualified a day for being a selected quiet day.   A gap in the secondary pulse columns other than $n+27$ and $n+28$ was filled by interpolation from the ranges of the adjacent days.   While it is only proper to mention these facts, it should be added that the defective days were so few that the exact procedure adopted could hardly matter.

Table V.—Negative Pulses.　Kew Declination Ranges.

Year.	Primary pulse.					Negative pulse.					
	n − 2.	*n* − 1.	*n*.	*n* + 1.	*n* + 2.	*n* + 25.	*n* + 26.	*n* + 27.	*n* + 28.	*n* + 29.	*n* + 30.
1858	1·46	4·08	7·16	3·73	+0·64	1·48	1·80	2·29	2·83	2·01	+0·45
1859	2·83	4·44	7·88	3·48	1·93	1·23	+0·59	+0·06	0·38	1·92	1·51
1860	0·17	3·02	7·66	2·72	0·92	+0·99	+1·20	+0·71	+0·98	0·77	+0·17
1861	2·49	4·14	7·18	2·23	+0·35	0·96	+0·20	0·53	+0·45	+2·02	+0·74
1862	+0·08	3·50	8·40	1·87	+1·57	1·27	2·18	1·08	+3·26	+0·50	+0·90
1863	2·66	4·12	8·06	2·14	+0·73	1·08	1·43	1·35	1·98	1·40	+0·17
1864	2·55	4·26	8·53	4·05	1·18	0·43	2·60	3·00	1·18	0·26	+1·00
1865	3·60	5·75	9·28	1·47	+2·06	1·39	2·19	3·09	2·30	1·20	+0·89
1866	2·40	3·12	7·98	3·78	+0·73	2·21	2·00	2·46	0·97	1·29	1·10
1867	1·60	3·16	6·02	2·56	0·51	1·30	1·62	2·81	0·45	+0·48	+0·09
1868	1·35	2·75	7·06	3·12	0·58	0·82	3·39	2·39	2·88	2·46	0·74
1869	0·15	4·36	8·14	4·76	1·67	+1·84	1·13	4·28	3·70	2·37	1·74
1870	1·13	2·52	7·98	2·35	1·07	+0·42	0·06	0·57	0·85	1·10	1·02
1871	0·31	2·66	7·56	2·23	+0·02	1·85	2·54	+0·30	+0·42	+0·54	+0·20
1872	1·92	4·47	8·60	2·66	+1·28	+1·05	2·14	3·85	3·08	+0·42	+2·56
1873	+0·57	1·72	5·91	0·33	+3·52	0·03	0·18	1·97	1·47	0·78	+1·00
1875	0·92	2·25	4·56	1·60	+0·35	1·10	1·13	0·59	0·86	+0·34	+1·56
1876	0·60	1·93	4·16	1·35	0·36	0·76	0·04	+1·09	0·28	0·50	0·48
1877	0·71	1·89	3·97	0·95	+0·69	+0·21	0·60	0·48	+0·27	+0·25	+0·19
1878	1·14	1·73	3·53	1·50	0·24	0·04	0·31	1·07	0·48	0·29	+0·19
1879	0·99	1·25	3·13	1·13	0·80	0·51	0·74	1·16	0·87	0·11	0·57
1880	+0·06	1·06	4·33	1·56	1·14	1·19	1·52	0·46	0·32	0·31	0·12
1881	+1·17	1·71	4·77	2·12	0·30	0·12	0·15	1·29	+0·60	+1·84	+1·35
1882	+0·45	2·38	7·28	2·44	+1·75	1·29	0·15	+0·42	0·29	2·25	+1·58
1883	1·02	2·16	6·44	1·87	+0·08	+0·79	1·67	1·75	1·77	+0·87	+0·94
1884	0·62	1·87	5·00	1·80	0·49	0·22	1·12	1·58	0·79	1·14	0·32
1885	0·26	2·32	5·18	1·64	0·10	0·47	0·02	0·80	+0·72	+0·08	0·82
1886	0·62	2·77	6·48	1·66	0·11	+0·33	0·89	2·10	1·30	1·25	+0·50
1887	0·74	2·83	5·37	2·30	0·14	0·54	1·19	1·41	1·21	1·08	+0·08
1888	1·64	2·90	5·30	1·26	0·14	1·42	2·21	1·48	1·16	+0·26	+1·17
1889	0·74	2·05	4·62	1·15	+0·26	0·65	1·13	1·26	0·63	+0·32	+0·62
1890	0·43	1·40	3·78	0·79	+0·26	0·46	0·12	0·66	0·23	0·37	0·64
1891	1·44	2·26	5·49	1·88	+0·79	0·80	1·29	0·77	+0·27	+1·43	
1892	+1·73	3·91	7·66	3·68	0·88	+0·42	+0·66	+0·89	+0·21	1·08	2·98
1893	0·52	2·19	5·38	2·01	+0·79	1·78	1·40	1·00	0·36	0·68	0·00
1894	1·31	3·23	6·66	2·33	0·26	+1·22	1·17	2·40	0·17	2·67	2·77
1895	0·46	2·31	6·29	1·80	+0·35	0·95	1·64	1·83	0·98	0·38	0·35
1896	1·80	3·18	6·11	1·50	0·48	1·04	2·25	2·91	2·05	1·44	0·61
1897	0·54	2·68	5·14	1·31	0·24	+0·04	1·48	0·34	0·36	+1·29	0·07
1898	1·96	2·53	5·28	2·60	1·60	2·00	1·36	2·59	0·93	0·59	0·44
1899	1·12	2·07	4·72	1·92	0·48	1·30	0·96	1·85	1·08	1·04	+0·44
1900	+0·05	1·17	3·37	1·22	0·34	+0·51	+0·50	+0·17	+0·54	0·32	0·23
Mean ...	0·95	2·76	6·18	2·12	+0·03	0·53	1·07	1·32	0·75	0·51	+0·04

Table IV gives the positive pulses derived from the 5 days of largest range in each month and associated days; a minus sign signifies that the mean range from the disturbed or associated days fell short of the mean range from all days. Table V gives the negative pulses derived from the 5 days of least range in each month and associated days; a plus sign signifies that the mean range from all days was exceeded. Table VI gives the difference pulses

Table VI.—Difference Pulses.   Kew Declination Ranges.

Year.	Primary pulse.					Secondary pulse.					
	$n-2$.	$n-1$.	n.	$n+1$.	$n+2$.	$n+25$.	$n+26$.	$n+27$.	$n+28$.	$n+29$.	$n+30$.
1858	1·36	8·24	20·92	8·24	−1·01	1·20	3·25	4·75	4·86	2·31	−0·68
1859	5·33	10·86	24·55	11·21	4·19	0·92	0·41	2·19	0·67	2·14	2·46
1860	1·64	9·55	22·35	6·59	1·29	−0·27	−0·38	−0·05	−0·99	0·05	−0·21
1861	2·44	10·67	21·69	7·26	1·84	2·04	3·00	2·81	1·24	−1·65	0·31
1862	−0·31	8·16	24·21	6·46	−2·37	3·66	3·45	2·16	−3·34	−1·61	0·26
1863	1·95	6·75	20·66	7·25	0·64	0·75	2·45	4·73	4·54	3·19	0·89
1864	3·61	10·05	22·67	9·88	3·18	1·86	6·20	6·85	4·73	4·00	0·76
1865	4·00	11·47	25·34	7·66	−0·47	0·89	5·36	8·10	8·36	2·83	−0·78
1866	1·27	6·96	20·76	8·34	−0·34	2·03	2·81	3·62	2·84	3·32	1·30
1867	3·07	6·48	17·40	7·76	2·24	3·48	4·98	6·63	3·69	2·52	1·66
1868	1·33	6·60	19·85	6·42	0·96	1·33	5·51	5·57	5·06	2·63	2·31
1869	−0·54	10·29	23·77	9·99	1·75	−1·57	0·33	5·22	6·81	3·18	1·58
1870	1·23	9·75	23·91	7·18	0·85	0·53	0·98	0·58	2·74	4·87	3·56
1871	−0·48	5·43	21·12	5·65	−1·46	1·49	4·64	−0·56	−0·50	−1·53	−0·29
1872	1·66	11·08	24·95	8·35	0·38	−1·27	4·36	5·08	5·78	1·90	−2·00
1873	−2·04	4·66	17·45	2·68	−3·01	−0·35	−0·30	1·83	2·99	1·87	−2·76
1875	−0·04	3·76	12·51	4·11	0·00	1·50	1·90	1·23	2·71	−0·23	−2·32
1876	−0·25	4·56	12·37	3·76	−0·30	1·00	−0·58	−0·28	1·22	1·22	0·42
1877	−0·17	4·20	11·71	3·57	−0·49	−0·16	2·82	2·09	0·62	−0·58	−1·06
1878	0·78	3·97	9·70	3·49	0·05	−0·51	0·66	2·22	1·01	−0·28	−0·28
1879	1·36	2·61	8·22	2·50	1·24	0·76	1·59	2·60	2·16	0·90	0·34
1880	0·66	3·33	12·59	4·13	1·23	1·66	2·42	1·66	1·55	0·47	−0·20
1881	−1·74	4·23	12·15	4·06	0·24	0·79	0·54	2·58	0·00	−1·13	−0·29
1882	−1·40	7·67	23·83	5·14	−1·91	−0·42	−0·14	0·12	−0·28	1·75	−1·43
1883	−0·04	6·05	17·97	5·13	1·11	−0·93	1·56	2·79	1·96	0·70	−0·11
1884	0·40	5·47	14·14	4·86	−0·41	−0·82	1·31	2·52	1·47	0·84	0·72
1885	0·44	4·56	14·74	4·35	0·76	0·59	0·51	1·81	0·65	1·30	1·52
1886	1·62	7·02	18·60	5·53	1·19	−0·76	3·26	6·37	6·29	3·42	0·85
1887	1·50	6·28	14·50	6·63	1·65	−0·09	2·65	3·79	4·94	3·42	0·87
1888	1·62	6·44	14·92	3·96	−0·05	1·42	4·58	4·83	3·40	−0·03	−2·02
1889	−0·29	3·36	12·50	3·06	0·55	0·24	1·65	4·40	2·55	−0·07	−1·32
1890	0·75	3·13	9·43	2·54	−0·05	0·37	0·81	1·29	0·69	1·14	1·79
1891	2·08	5·51	15·82	5·62	1·21	0·71	3·08	1·78	3·47	1·43	−0·96
1892	−3·27	10·21	24·70	8·88	1·43	−1·75	−1·98	1·02	1·08	1·61	0·90
1893	0·38	4·76	18·98	4·89	−0·23	1·60	1·69	1·80	1·97	1·46	0·50
1894	0·40	6·97	21·95	7·64	1·17	−2·49	1·19	2·35	0·76	3·88	5·45
1895	0·47	4·67	16·43	5·31	1·18	0·15	2·16	4·94	3·30	3·18	2·05
1896	2·45	7·32	17·77	7·38	3·09	2·81	5·12	6·51	5·89	4·34	1·16
1897	−0·83	5·30	14·35	3·55	−0·38	−0·32	2·56	1·95	1·61	−1·61	1·00
1898	2·14	7·17	15·97	6·13	1·99	2·66	2·09	5·22	3·67	3·33	1·12
1899	0·79	4·75	13·29	4·49	1·33	1·82	3·37	4·11	2·49	1·09	−0·59
1900	−0·27	2·61	8·60	1·88	0·17	−0·20	0·51	0·13	−0·56	0·22	0·94
Mean (42 yrs.)	0·83	6·52	17·47	5·80	0·58	0·63	2·20	3·08	2·47	1·47	0·41

representing the mean excess in range of the days of large range or associated days over the days of small range or associated days; a minus sign implies that the mean range from the days associated with the days of largest range was the smaller.

It will be noticed that the majority of the entries in column $n-2$ of Table IV have the minus sign, and that a plus sign occurs with nearly half

Table VII.—Kew Declination Ranges. Groups of Years.

	Years.	Primary pulse.					Secondary pulse.						S/P.	S/P'.
		$n-2$.	$n-1$.	n.	$n+1$.	$n+2$.	$n+25$.	$n+26$.	$n+27$.	$n+28$.	$n+29$.	$n+3\,0$.		
Large ranges	All	−0·13	3·75	11·84	3·68	0·61	0·10	1·13	1·76	1·72	0·96	0·45	0·16	0·25
	A	−0·18	5·04	13·98	4·41	0·67	−0·31	0·63	1·10	1·08	0·85	0·64	0·08	0·13
	B	−0·16	2·48	8·12	2·67	0·41	0·14	1·29	1·83	1·54	0·76	0·15	0·23	0·35
	C	−0·17	4·37	12·25	3·75	0·43	0·00	0·64	1·35	1·22	0·67	0·37	0·11	0·16
	D	−0·30	3·25	9·52	3·14	0·37	−0·06	1·57	2·14	2·07	0·77	0·16	0·22	0·36
Small ranges	All	0·95	2·76	6·13	2·12	+0·03	0·53	1·07	1·32	0·75	0·51	+0·04	0·22	0·29
	A	0·77	3·12	7·12	2·60	0·18	0·11	0·74	1·10	0·74	0·75	0·33	0·15	0·20
	B	1·01	2·13	4·66	1·66	0·09	0·71	0·87	1·12	0·55	0·31	0·02	0·24	0·32
	C	0·50	2·70	6·33	2·60	0·44	0·32	0·62	0·91	0·88	0·97	0·34	0·15	0·24
	D	1·38	2·67	5·39	1·83	+0·03	0·81	1·17	1·46	0·77	0·40	+0·11	0·27	0·35
Difference pulses	All	0·83	6·52	17·47	5·80	0·58	0·63	2·20	3·08	2·47	1·47	0·41	0·18	0·26
	A	0·59	8·16	21·10	7·01	0·80	−0·20	1·87	2·20	1·82	1·60	0·96	0·10	0·15
	B	0·84	4·61	12·79	4·33	0·50	0·85	2·16	2·95	2·09	1·07	0·17	0·23	0·33
	C	0·68	7·08	18·58	6·35	0·88	0·33	1·26	2·25	2·10	1·64	0·71	0·12	0·19
	D	1·08	5·92	14·91	4·97	0·35	0·75	2·74	3·61	2·84	1·17	0·03	0·24	0·36

the entries in column $n + 2$ of Table V. There are, however, an appreciable number of minus signs in column $n + 2$ of Table IV, and of plus signs in column $n - 2$ of Table V. Thus, while there is asymmetry similar to that in Tables I and II, it is less marked.

Sometimes a range exceeding the mean for the month was observed in a decidedly quiet day, and in one or two exceptionally quiet months the selected days of largest range included a day of this character. But the very large majority of the selected days of largest range were amongst the most disturbed days of the month. A small range might mean that disturbing forces were present, but happened to oppose the ordinary diurnal variation. This may have occurred in a few cases, but the selected days of least range undoubtedly represented in all months a much quieter set of conditions than the average day.

The mean results from the whole 42 years are given in the last lines of Tables IV, V, and VI. All show a well developed secondary pulse, the entry in column $n + 27$ being the largest. In Table IV the excess of the entry in column $n + 27$ over that in column $n + 28$ is small. Also the primary pulse is nearly symmetrical about column n, much more nearly so than the primary pulse in Table I; thus the period suggested is very decidedly in excess of 27 days. The negative pulses in Table V show a close parallelism to those in Table II, and suggest a period of very nearly 27 days. In Table VI the crest of the primary difference pulse seems slightly in advance of column n, and the crest of the secondary difference pulse slightly later than column $n + 27$, so that a period slightly in excess of 27 days is indicated.

§ 5. Before considering individual years, it is desirable to consider the results for the four groups of years in Tables I, II, III, and VII. The groups of years A, B, C, D were made up as follows, the first set of data in each case referring to the earlier period 1858–1900, the second to the later period 1906–1920.

For the information in the last column I am indebted to the Astronomer Royal, and to a paper by Mr. E. W. Maunder.[*]

There is a close relationship, at least approximately linear, between the range of the regular diurnal inequality of D (or other magnetic element) and sunspot frequency, the range being much larger in years of many than in years of few sunspots. The relationship of disturbance to sunspot frequency is less definite. Sunspot minimum is usually a very quiet time. Some years of great sunspot development are not specially disturbed, but most years of large sunspot frequency are more disturbed than the average year. Thus we should expect the amplitudes of the primary pulses to be above the average in the groups A, and below the average in groups B, and this is what we

[*] 'R. A. S. Notices,' vol. 74, p. 112.

Group.	Number of years.	Individual years.	Sunspot data.	
			Wolfer's frequency.	Mean equatorial distance.
A {	14	1859, '60, '61, '69, '70, '71, '72, '82, '83, '84, '92, '93, '94, '95	84·2	15·9
	5	1906, '07, '17, '18, '19	72·8	P
B {	12	1866, '67, '76, '77, '78, '79, '87, '88, '89, '90, '99, 1900	9·3	11·5
	4	1911, '12, '13, '14	5·1	14·9
C {	13	1858, '59, '60, '68, '69, '70, '79, '80, '81, '82, '90, '91, '92	58·7	19·7
	3	1913, '14, '15	19·5	21·3
D {	10	1865, '66, '77, '78, '87, '88, '97, '98, '99, 1900 ...	15·7	8·8
	5	1908, '09, '10, '11, '12	24·1	9·0

actually observe in Tables I, II, and III, and to a more marked extent in Table VII. But it is very different with the secondary pulses. In spite of the diminished amplitude of the primary positive pulse in sunspot minimum years, the amplitude of the secondary positive pulse in Tables I and VII is much larger for group B than for group A years. The same is true of the difference pulses in Tables III and VII. Absolutely considered, the amplitude of the secondary negative pulse is much the same for group A and group B years in Tables II and VII, but the values of S/P and S'/P' are much larger for the sunspot minimum groups. The groups C and D of high and low spot latitude years employed in Tables I, II, and III differ little in mean sunspot frequency, and the primary pulses reflect this approach to equality. The amplitude of the secondary pulse is decidedly larger for the D group in all three Tables, and the values of S/P and S'/P' for this group are also decidedly the larger in Tables I and III.

In Table VII the C group had a much higher mean sunspot frequency than the D group, and this is reflected in the higher amplitude of the primary pulses of the former group. But in spite of this the secondary pulses associated with the D group are all much the larger. The values of S/P, in fact, for both the positive and difference pulses, are twice as large for the D as for the C group.

In view of the much larger number of years it is based on, we should naturally assign more weight to Table VII than to Tables I, II, and III, and hence conclude that low sunspot frequency and a low latitude of spots both conduce to the development of the 27-day period.

§ 6. The primary object in forming groups C and D was to see whether the interval between the crests of the primary and secondary pulses differed sensibly in years of high and low sunspot latitude. Mr. and Mrs. Maunder[*] give two tables for the synodic periods of sunspots in zones of different latitudes. The second Table, confined to recurrent spots, gives values very sensibly greater, especially for low latitudes, than the first Table, which includes short-lived spots. The recurrent spot data seem clearly those appropriate in the present case. From these we should infer synodic periods of 26·9, 27·2, and 27·3 days respectively for solar latitudes of 9°, 20°, and 21°. Thus the synodic period should be from 0·3 to 0·4 days longer for the group C than the group D years. The question is whether any such difference occurs in the interval between the crests of the primary and secondary pulses of magnetic " character," or range, in groups C and D ?

There is a slight suggestion of a difference in the direction indicated in the case of the negative pulses in Table II, but Table I points the other way, the excess in the entry in column $n + 28$ over that for column $n + 26$ being largest in the D group. In Table III, the C.G. of the secondary pulse seems a shade later in the D than in the C group, but the same is true of the primary pulse. There is no clear variation in the interval, and certainly no suggestion of a difference as large as 0·4 day.

In Table VII, the interval between the crests of the primary and secondary positive pulses seems as nearly as possible the same for groups C and D. The secondary negative pulse for group C has a nearly flat top. If there is a single maximum, it would seem to fall decidedly later than in the D group; but this is compensated to some extent by the earlier occurrence of the primary crest in the latter group. In the case of the difference pulses the interval between the crests does seem sensibly longer for the C group, and the difference in length might be as large as 0·3 day. But, however this may be, it seems clear that the interval for the D group is in excess of 27 days, and not less.

In considering this question importance attaches to a result emphasised by Mr. and Mrs. Maunder, viz., that whilst the synodic period increases steadily with the latitude, when we take mean figures from a large number of spots, a considerable range of period is observed in spots having the same latitude. If only a moderate percentage of all the spots were effective for disturbing the earth's magnetic field, it might happen, at least in an individual year, that the mean synodic period of those effective differed very sensibly from the period appropriate to the mean spot latitude of the year. This in fact would be more than a possibility if the percentage of spots that are effective

[*] 'R. A. S. Notices,' vol. 65, p. 813.

increased as the latitude diminished.   In that event the synodic period of the average effective spot would naturally be shorter than the mean spot latitude of the year.

In view of the interest which this question possesses in connection with theories which suppose sunspots ˙to be the actual sources of electrical discharges causing magnetic storms,[*] it seemed worth while to consider the apparent variations in the position of the maximum of the secondary pulse in individual years.   We must expect a considerable accidental element, so that what we have to consider is whether the majority of the years in which the period is specially long or specially short have any common sunspot characteristic.   As the primary difference pulse is the most symmetrical, and the secondary difference pulse is that least exposed to accidental features, attention is confined to it.

Considering Tables VI and III we find the interval to be 28 days or more in the years 1858, '65, '69, '70, '72, '73, '75, '76, '82, '87, '91, '92, '93, '94, 1909 and 1914, and 26 days or less in 1861, '62, '71, '77, '80, '97, 1908 and 1917.

There does not seem any approach to a common characteristic in either group.   Both contain years of many and years of few spots, and also years of high and years of low latitude.

§ 7. The years in which the 27-day period is best displayed include 1858, '63, '64, '65, '67, '68, '69, '72, '86, '87, '88, '89, '95, '96, '98, '99, 1910, '11, '13, '15 and '20.   These are mostly years when spot latitudes were low, but there are notable exceptions to this including 1858, 1868, 1869 and 1913.   Amongst the earlier group of years 1865 is pre-eminent, and amongst the later years 1911.

The years in which the 27-day period is least apparent include 1860, '71, '76, '82, '85, '90, '92, 1900, '07, '09, '14 and '16.

The failure of the secondary negative pulse in 1860 was mainly due to the fact that the 27-day followers of three of the days of least range in July belonged to a series of seven consecutive days of large disturbance.   In 1882 the largest range of the year (2° 18·0′) occurred on a day which was a 27-day follower of one of the selected days of least range, and the next highest range (2° 12·2′) occurred on a 28-day follower.   These were amongst the largest ranges of the 42 years.   But for their "chance" occurrence, the year 1882 would have exhibited a normal negative pulse.   An "accident" of this kind

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* Since the preparation of this paper was completed a paper has appeared in the ' R. A. S. Notices ' (vol. 82, p. 170), by the Rev. A. L. Cortie, who claims to have found a close agreement between the synodic periods of sunspots in different latitudes and the "repetition" periods derived from certain magnetic storms which he associates with the sunspots.   His synodic periods seem decidedly in excess of those given by Mr. and Mrs. Maunder for the same latitudes.

is much more fatal to the secondary pulse than is the corresponding " accident "
of days of small range being followers of days of large range. These
"accidents " may, however, be less fortuitous than we should naturally suppose.
At all events, it will be seen that years in which the negative secondary
pulse was badly developed showed also as a rule poorly developed positive
secondary pulses.

§ 8. For the consideration of the annual variation in the 27-day period, a
knowledge is desirable of the mean " character," figures, and mean ranges, for
the 12 months, derived from all the years combined. These are as follows :—

	" Character." 1906–1920.	D. range. 1858–1900.
January	0·618	12·07
February	0·679	14·53
March	0·709	16·40
April	0·623	16·87
May	0·632	14·93
June	0·553	14·68
July	0·561	14·85
August	0·659	16·12
September	0·698	16·28
October	0·695	15·92
November	0·602	13·41
December	0·590	10·93

In both cases there is a double oscillation, with maxima towards the
equinoxes and minima near the solstices. The chief difference is that June
shows the lowest " character," December the lowest range. But the absolute
range, as stated above, is partly determined by the regular diurnal variation,
and the amplitude of the diurnal inequality is much larger at Kew (a northern
station) in June than in December. The character of an individual month,
as regards disturbance, cannot, of course, be safely deduced from the five most
disturbed days. Table VIII represents, however, mean results from the
selected disturbed days of 15 years. Thus one would expect a fairly close
parallelism between the annual variation in the amplitude of the primary
pulse in Table VIII, and the variation shown above in the mean " character "
figures for the 12 months. In both cases, when the months are arranged
according to amplitude, the equinoctial months March, September, and
October, come at the top, and June at the foot. The order of the intermediate
months differs considerably in the two cases, but the differences between the
figures for August, May, April, July, and January, in Table VIII, are so small
that the precise order in which these months occur possesses little significance.
The chief difference is as regards February, on the one hand, and November
and December on the other. February would seem to be a month when

disturbances are numerous but few outstanding, while November and December are months in which the largest disturbances overshadow the others.

The amplitudes of the primary negative pulse in Table IX, and of the primary difference pulse in Table X, show at least as close a parallelism in their annual variation to the mean " character " figures as does the amplitude of the positive pulse, July falling to the second lowest place, and November and December coming nearer the foot.

If the months were arranged according to the amplitude of the primary D pulse, their order would be precisely the same in Tables XI and XIII. October, November, February, and March, coming at the top, in the order stated, and August, May, July, and June, coming at the bottom. The order in Table XII would be only slightly different.

The annual variation in the amplitude of the primary difference pulses in Tables X and XIII shows a very regular progression. In both cases, too, we have a minimum in June and a maximum in October. Table XIII differs from Table X chiefly in that November and February come more to the front, while September and March retire.

All the months in Tables VIII, IX, XI, and XII show distinct secondary pulses; the 27-day period is clearly existent in all months of the year. The incidence of the crest of the secondary pulse seems, however, rather irregular, especially that of the negative pulse. This phenomenon, especially in the case of the D range, is probably, in part, an indirect consequence of the considerable amplitude of the annual range. Take, for instance, the D range phenomena associated with the January primary pulses. The range is naturally rising during the occurrence of the secondary pulses. For absolute accuracy the normal range should rise gradually from column $n + 25$ to column $n + 30$, while the mean value for February has been used in all these columns. The natural consequence of this would be a gradual algebraical increase from column $n + 25$ to column $n + 30$ of the positive pulse, and a corresponding numerical fall in the negative pulse. This, it will be seen, is what the negative pulse actually shows, though this may not be the only cause of the phenomenon. The difference pulses should be free from this defect, and they are, in fact, much more regular. The maximum in the secondary pulse appears in column $n + 27$ in 9 months out of the 12 in both Tables X and XIII. In Table X the maximum is found twice in column $n + 26$, and once in column $n + 28$. In Table XIII it occurs thrice in column $n + 28$. The exceptions occur in only one case in the same month, January, and the excess of the entry in column $n + 28$, over that in column $n + 27$ in the January figures in Table X, is trifling. There is thus no real indication of a seasonal variation in the length of the period.

Table VIII.—Positive Pulses. International "Character" Figures. Annual Variation.

| Month. | Primary pulse. | | | | | Secondary pulse. | | | | | | S/P. | S'/P'. |
	n−2.	n−1.	n.	n+1.	n+2.	n+25.	n+26.	n+27.	n+28.	n+29.	n+30.		
January	0·063	0·243	0·665	0·365	0·178	0·033	0·134	0·182	0·192	0·125	0·076	0·29	0·40
February	−0·004	0·287	0·634	0·348	0·138	0·015	0·064	0·163	0·122	0·094	0·062	0·26	0·31
March	−0·063	0·402	0·734	0·427	0·168	0·064	0·176	0·206	0·140	0·128	0·134	0·28	0·33
April	−0·055	0·298	0·674	0·302	0·086	0·073	0·101	0·104	0·099	0·019	−0·037	0·15	0·24
May	0·011	0·312	0·676	0·380	0·093	0·072	0·159	0·211	0·175	0·043	−0·042	0·31	0·40
June	−0·010	0·351	0·628	0·364	0·148	−0·036	0·032	0·110	0·072	0·014	0·022	0·18	0·16
July	−0·037	0·234	0·672	0·332	0·076	0·014	0·069	0·185	0·170	0·110	0·028	0·28	0·38
August	−0·084	0·245	0·689	0·342	0·021	−0·011	0·147	0·209	0·113	0·054	0·014	0·30	0·37
September	−0·007	0·289	0·718	0·387	0·142	0·029	0·086	0·244	0·217	0·180	0·086	0·34	0·46
October	0·084	0·297	0·736	0·452	0·177	0·043	0·139	0·153	0·166	0·099	0·081	0·23	0·31
November	−0·019	0·267	0·706	0·330	0·066	−0·038	0·085	0·127	0·097	0·033	0·039	0·18	0·24
December	0·018	0·314	0·705	0·322	−0·025	−0·076	0·033	0·169	0·119	0·079	−0·001	0·24	0·27
Mean ratios												0·25	0·32

Table IX.—Negative Pulses. International "Character" Figures. Annual Variation.

| Month. | Primary pulse. | | | | | Secondary pulse. | | | | | | S/P. | S'/P'. |
	n−2.	n−1.	n.	n+1.	n+2.	n+25.	n+26.	n+27.	n+28.	n+29.	n+30.		
January	0·018	0·287	0·523	0·139	+0·043	+0·017	0·039	0·038	0·038	0·066	0·106	0·20	0·22
February	0·064	0·258	0·539	0·184	+0·077	0·105	0·217	0·224	0·073	0·061	0·045	0·42	0·56
March	0·170	0·374	0·605	0·321	+0·008	0·063	0·199	0·196	0·108	0·009	+0·057	0·33	0·39
April	0·107	0·294	0·539	0·231	0·020	0·105	0·092	0·063	0·055	+0·004	0·009	0·19	0·25
May	0·060	0·284	0·501	0·233	0·088	0·053	0·140	0·122	0·062	0·001	+0·046	0·28	0·32
June	0·102	0·289	0·469	0·218	+0·084	0·076	0·152	0·144	0·061	0·008	0·010	0·32	0·38
July	0·124	0·309	0·491	0·229	0·068	0·018	0·022	0·096	0·090	0·078	0·107	0·22	0·26
August	0·055	0·303	0·556	0·224	+0·042	0·134	0·166	0·174	0·137	0·095	0·050	0·31	0·44
September	0·113	0·341	0·589	0·207	+0·057	0·103	0·078	0·155	0·147	0·096	+0·013	0·26	0·35
October	0·191	0·388	0·603	0·279	0·070	0·195	0·185	0·142	0·025	+0·013	+0·030	0·32	0·41
November	0·051	0·277	0·497	0·257	+0·075	+0·073	+0·001	0·114	0·129	0·093	0·026	0·26	0·33
December	0·102	0·303	0·502	0·191	0·037	0·027	0·117	0·231	0·186	0·043	+0·120	0·46	0·49
Mean ratios												0·30	0·37

Table X.—Difference Pulses.　International "Character" Figures.　Annus Variation.

Month	Primary pulse					Secondary pulse						S/P.	S/P'.
	n−2.	n−1.	n.	n+1.	n+2.	n+25.	n+26.	n+27.	n+28.	n+29.	n+30.		
January	0·080	0·530	1·188	0·504	0·135	0·016	0·173	0·220	0·230	0·191	0·182	0·19	0·29
February	0·060	0·495	1·172	0·532	0·061	0·120	0·281	0·387	0·195	0·155	0·107	0·33	0·39
March	0·233	0·776	1·389	0·748	0·158	0·127	0·375	0·402	0·248	0·119	0·077	0·30	0·36
April	0·052	0·592	1·213	0·533	0·106	0·178	0·193	0·172	0·154	0·015	−0·028	0·16	0·23
May	0·071	0·596	1·177	0·613	0·181	0·125	0·299	0·333	0·237	0·044	−0·088	0·28	0·37
June	0·092	0·640	1·096	0·582	0·064	0·040	0·184	0·254	0·133	0·022	0·032	0·23	0·25
July	0·087	0·543	1·153	0·561	0·144	0·032	0·091	0·281	0·250	0·188	0·135	0·24	0·32
August	−0·009	0·548	1·245	0·566	−0·021	0·123	0·313	0·383	0·250	0·149	0·064	0·31	0·40
September	0·106	0·630	1·307	0·594	0·085	0·132	0·164	0·399	0·364	0·276	0·073	0·31	0·41
October	0·255	0·685	1·389	0·731	0·247	0·238	0·324	0·295	0·191	0·086	0·051	0·24	0·31
November	0·032	0·544	1·203	0·587	−0·009	−0·111	0·084	0·241	0·226	0·126	0·065	0·20	0·25
December	0·120	0·617	1·207	0·513	−0·062	−0·049	0·150	0·400	0·255	0·036	−0·121	0·33	0·34
Mean ratios												0·26	0·33

Table XI.—Positive Pulses.　Kew D Ranges.　Annual Variation.

Month	Primary pulse					Secondary pulse						S/P.	S/P'.
	n−2.	n−1.	n.	n+1.	n+2.	n+25.	n+26.	n+27.	n+28.	n+29.	n+30.		
January	−0·65	3·65	12·21	4·32	1·64	−0·73	−0·41	0·99	2·50	1·43	1·31	0·20	0·26
February	0·11	5·35	13·54	5·32	1·10	0·20	1·42	1·62	1·25	0·92	0·67	0·12	0·18
March	−0·72	3·69	12·25	3·63	−0·60	0·20	1·53	2·68	2·36	0·77	−0·19	0·22	0·34
April	−0·41	4·06	11·25	2·99	−0·40	0·09	1·29	1·89	1·75	0·70	0·08	0·17	0·27
May	−0·22	2·91	9·21	2·95	0·55	−0·01	0·67	1·74	1·19	0·30	0·46	0·19	0·24
June	−0·55	2·25	7·42	2·17	0·02	−0·03	0·69	0·90	0·71	0·24	0·23	0·12	0·19
July	0·26	2·87	8·42	2·13	0·96	−0·70	0·58	1·08	0·67	0·76	0·00	0·12	0·18
August	0·06	2·47	10·27	2·96	0·67	0·33	0·94	1·12	1·32	0·66	0·72	0·13	0·22
September	−0·11	4·06	11·95	3·87	0·03	0·46	2·19	2·52	2·25	1·62	0·68	0·21	0·35
October	0·71	4·51	13·83	4·81	1·48	0·15	2·57	2·52	2·49	1·84	0·91	0·19	0·33
November	0·01	5·65	13·71	4·94	1·29	1·58	1·81	2·70	2·50	1·91	0·90	0·20	0·29
December	−0·21	3·31	11·91	3·98	0·30	−0·61	−0·06	1·25	1·56	1·20	0·10	0·13	0·21
Mean ratios												0·17	0·25

Table XII.—Negative Pulses. Kew D Ranges. Annual Variation.

Month.	Primary pulse.					Secondary pulse.						S/P.	S'/P'.
	$n-2$.	$n-1$.	n.	$n+1$.	$n+2$.	$n+25$.	$n+26$.	$n+27$.	$n+28$.	$n+29$.	$n+30$.		
January	2·11	3·86	6·76	1·66	+0·07	2·18	1·99	1·97	1·81	1·17	+0·26	0·32	0·48
February	1·76	3·99	7·53	3·66	0·77	1·99	2·51	2·51	2·19	0·58	0·65	0·33	0·47
March	1·45	3·25	6·93	2·86	1·31	+0·65	0·34	0·62	+0·14	0·04	0·13	0·09	0·07
April	0·06	2·05	5·66	2·49	0·06	0·25	0·55	0·73	0·48	0·48	0·12	0·13	0·17
May	0·36	1·91	5·07	2·01	0·77	0·28	0·78	0·83	0·48	1·05	0·43	0·21	0·26
June	0·36	1·19	4·33	1·48	0·04	0·21	0·37	0·98	0·87	0·51	0·24	0·23	0·34
July	+0·12	1·86	4·76	1·64	+0·03	+0·07	0·78	1·28	0·34	0·14	+0·20	0·27	0·31
August	1·03	2·41	5·70	1·57	+0·20	0·34	0·79	0·81	0·71	0·43	+0·42	0·14	0·24
September	1·03	3·25	6·47	2·69	+0·19	0·48	1·23	2·13	1·03	0·73	+0·11	0·33	0·35
October	2·17	3·85	7·41	2·53	+0·76	0·19	0·98	0·86	1·09	1·38	+0·74	0·18	0·24
November	1·44	4·02	7·49	2·63	+0·60	0·34	1·64	1·64	0·89	+0·13	+0·33	0·22	0·29
December	0·51	2·83	6·29	1·62	+0·38	1·19	1·35	1·87	+0·56	0·13	0·43	0·30	0·41
Mean ratios												0·23	0·30

Table XIII.—Difference Pulses. Kew D Ranges. Annual Variation.

Month.	Primary pulse.					Secondary pulse.						S/P.	S'/P'.
	$n-2$.	$n-1$.	n.	$n+1$.	$n+2$.	$n+25$.	$n+26$.	$n+27$.	$n+28$.	$n+29$.	$n+30$.		
January	1·45	7·51	18·97	5·98	1·57	1·45	1·57	2·95	4·30	2·59	1·05	0·23	0·30
February	1·88	9·34	21·08	8·98	1·88	2·19	3·93	4·12	3·43	1·51	1·32	0·20	0·29
March	0·73	6·94	19·18	5·79	0·71	-0·44	1·90	3·31	2·22	0·81	-0·06	0·17	0·23
April	-0·35	6·12	16·91	5·48	-0·34	0·35	1·84	2·62	2·21	1·18	0·20	0·15	0·23
May	-0·14	4·82	14·28	4·96	1·32	0·26	1·44	2·58	1·67	1·35	0·89	0·18	0·24
June	-0·19	3·44	11·75	3·65	0·06	0·18	1·06	1·87	1·58	0·75	0·47	0·16	0·24
July	0·14	4·24	13·18	3·78	0·93	-0·77	1·36	2·31	1·01	0·90	-0·19	0·18	0·22
August	1·08	4·88	15·96	4·53	0·47	0·67	1·72	1·93	2·04	1·08	0·30	0·13	0·22
September	0·92	7·30	18·42	6·55	-0·17	0·94	3·42	4·65	3·28	2·35	0·58	0·25	0·35
October	2·86	8·36	21·24	7·83	0·72	0·34	3·55	3·38	3·57	3·20	0·18	0·17	0·28
November	1·44	9·67	21·20	7·57	0·68	1·93	3·45	4·34	3·39	1·78	0·57	0·20	0·29
December	0·30	6·14	18·20	5·60	-0·08	0·58	1·29	3·12	1·00	1·33	0·53	0·17	0·18
Mean ratios												0·18	0·26

In both Tables X and XIII the amplitude is large in the secondary pulses associated with February, March, and September, and low in those associated with June and July. The secondary pulse, of course, occurs nearly a month later than the primary pulse with which it is associated. The annual variation in the amplitude of the secondary pulse is most regular in Table XIII, where it follows, on the whole, the variation in the primary pulse.

The values of S/P and S'/P'—quantities having the same significance as in the earlier Tables—are slightly less for summer than the other seasons in Table XIII. If the southern hemisphere were as strongly represented as the northern in the international lists, there should be no sensible difference between summer and winter in Table X, and as a matter of fact high and low values of S/P and S'/P' occur rather promiscuously in that Table.

The variation in the position of the earth relative to the sun during its annual path has a marked effect on the amount of magnetic disturbance existing on the earth, but it seems to have little if any effect on the development of the 27-day period.

§ 9. In all terrestrial latitudes, so far as is known, the amplitude of the regular diurnal magnetic variation rises and falls with sunspot frequency. Again, it has been found that at least in high terrestrial latitudes the amplitude of the regular diurnal variation and the intensity of disturbance rise and fall together. It is thus natural to suppose that the increased amplitude of the regular diurnal variation in years of many sunspots is due to a solar radiation of the same type as the solar radiation causing magnetic disturbance or a very similar type. The difference very likely is merely in the regularity of the solar discharge. In years of many sunspots the large daily magnetic range is not a spasmodic feature. Small ranges, such as we meet with near sunspot minimum, simply do not exist. Consequently the solar discharge which influences the regular diurnal variation must be constantly operative. There is thus really nothing remarkable in the conclusion to which the present investigation points, viz., that it is not a question between magnetic storms and magnetic calms, but simply of disturbance above and below the average (*i.e.*, irregularity of solar discharge).

On the restricted view that magnetic storms are unique events, due to electrical discharges confined to sunspot areas, the existence of a 27-day period is an obvious corollary. But the existence of such a period does not by itself justify the conclusion that sunspots are the only sources, or even the principal sources, of the solar discharge. We should clearly still get a 27-day period if the whole solar surface were discharging, provided the discharge reaching the earth at any given instant came from a comparatively narrow zone, and the intensity were a function of the solar longitude which did not

vary two rapidly with the time. The period would naturally be less variable than if the radiation emanated only from isolated sunspots, but it might vary considerably if the latitude of most intense radiation varied.

Sunspots may be sources of specially vigorous solar discharges, or they may simply be symptoms that the sun is at the moment or recently has been specially active. Even in the quietest of years, and in the absence of visible sunspots, we have variations in the daily D range, and also at least minor disturbances; and, as the present investigation has conclusively shown, the 27-day period may be not merely recognisable but actually prominent in such a year. In fact 1913, with the lowest sunspot frequency since 1858, had the 27-day period particularly well developed.

It remains to express my indebtedness to the Government Grant Committee for the funds which rendered possible the measurement of the Kew declination ranges from 1858 to 1889. I have also to thank the Astronomer Royal for valuable information about sunspots and for useful references.

On Doubly-Resonated Hot-Wire Microphones.

By E. T. PARIS, M.Sc., Fellow of University College, London.

§ 1. *Introduction.*—In the selective hot-wire microphone[*] a Helmholtz resonator is used for the detection of sound-waves of definite pitch. The resonator responds to the particular note to which it is tuned, and its response is measured by the change in resistance of an electrically heated platinum-wire grid mounted in the "neck" of the resonator.

The magnitude of the response depends in the usual manner on the tuning and damping of the receiving system, and therefore in order to obtain great sensitivity the damping must be small and consequently the resonance must be sharp. For some purposes, however, sharp resonance may be a disadvantage— as, for example, when the source of sound is liable to small variations in pitch, or when allowance must be made for the Doppler effect—while at the same time it may be desired to retain a high degree of sensitivity. Even in cases where very sharp tuning is permissible, the only effective means of increasing the acoustical sensitivity is by reducing the neck of the resonator, and since

this tends to expose the hot-wire grid to chance currents of air, accurate observation becomes difficult except under very favourable conditions. To meet such difficulties as these, it has been found convenient to use doubly-resonated microphones in which the hot-wire grid is placed in a short neck between two resonators, only one of which communicates directly with the outside air. In this way it is possible to increase the range of response, and at the same time to obtain greater sensitivity than is practicable with a singly-resonated microphone.

This combination of a double resonator with the hot-wire grid, to form a very sensitive microphone, is due to Prof. H. L. Callendar, who carried out experiments early in 1918 to show how the component resonators could be arranged in order to secure a high degree of sensitivity together with a wide range of response.

In Prof. Callendar's experiments the neck of the singly-resonated microphone was inserted into a small hole at the closed end of a resonator of the " stopped pipe " variety. This arrangement was found to be very effective. About the same time, experiments along similar lines were being conducted by Major W. S. Tucker, R.E., who was then in charge of the Acoustical Research Section of the Munitions Inventions Department. In Major Tucker's experiments the neck of a Helmholtz resonator was inserted into a small hole at the narrow end of a conical trumpet. This arrangement also formed a double resonator which differed from that used by Prof. Callendar in that the outer resonator was a cone instead of a parallel pipe.

Since the time when these experiments were performed, the author, working with Major Tucker—first in the Munitions Inventions Department and later at the Signals Experimental Establishment, Woolwich—has had occasion to carry out a number of experiments with double resonators, and to study their properties by means of the hot-wire microphone. It is the purpose of the present paper to give an account of these investigations.

Reference may be made here to a very sensitive instrument constructed by Prof. C. V. Boys[*] in 1890, consisting of a double resonator fitted with a Rayleigh disc. In this instrument, according to Rayleigh—

> ".the sensitiveness is exalted to an extraordinary degree. This is effected . . . . partly by the adoption of double resonance. The large resonator is a heavy brass tube of about 10 cm. diameter, closed at one end, and of such a length as to resound to e'. The mirror [Rayleigh's disc] is hung in a short lateral tube forming a communication between the large resonator and a small glass bulb of suitable capacity. The

* 'Nature,' vol. 42, p. 604 (1890).

external vibrations may be regarded as magnified first by the large resonator and then again by the small one, so that the mirror is affected by powerful alternating currents of air. The selection of pitch is so definite that there is hardly any response to sounds which are a semi-tone too high or too low." *

Thus the double resonator used by Boys consisted of an outer resonator of the "stopped pipe" variety, communicating near the closed end with a Helmholtz resonator, as in Prof. Callendar's experiments. The properties of this type of double resonator—which for the convenience of reference will be called the "Boys double resonator"—are discussed in §§ 2–6 of the present paper. It may be noted here, in regard to the statement as to the definiteness of the pitch selected by Boys' resonator, that in general all such resonators have *two* natural tones. Under certain conditions, however, when the interval between the tones is large, the response may be much stronger to one tone than to the other. When this is the case, the resonator is often remarkably sensitive to the stronger tone, while the weaker one might even escape detection. The double resonator constructed by Boys appears to have been of this kind.

The present paper deals with the properties of two kinds of double resonator, namely, the Boys resonator (§§ 2–6), and a type which will be called the "Helmholtz double resonator" (§§ 7–10). The latter consists of inner and outer resonators communicating through a narrow tube or neck as in the Boys resonator, but both the components are of the Helmholtz pattern. The theory of this double resonator received attention from the late Lord Rayleigh.

In the experimental investigation of the behaviour of these resonators, the microphone grid was placed in the short neck joining the inner and outer resonators. The grid formed one arm of a Wheatstone bridge, and the response of the resonator was measured by the deflection of a galvanometer. The deflection was, in all cases, very closely proportional to the average fall in resistance of the microphone grid. It is known† that this fall in resistance is proportional to the energy of the vibratory motion of the air surrounding the grid, provided that the amplitude of the motion is not too great.

§ 2. *Theory of the Boys Double Resonator.*—This type of double resonator consists essentially of two parts :—

> (i) A resonator of the "stopped-pipe" variety, and
> (ii) A resonator of the Helmholtz pattern.

* 'Theory of Sound,' 2nd ed., vol. 2, p. 45.
† Tucker and Paris, *loc. cit.*, p. 410.

These are combined by inserting the neck of the Helmholtz resonator into a small hole in the stopped end of the pipe resonator.   The arrangement is shown diagrammatically in fig. 1, where P is the pipe resonator and Q the

Fig. I.
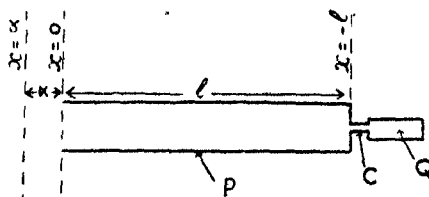
Helmholtz resonator, communication between the two taking place through the short neck c, in which also is placed the hot-wire grid.

Such an arrangement has two resonant tones, which may be near together, or far apart, according to the relative dimensions of the various parts of the resonator.   A formula will first be obtained which gives the frequencies of the resonant tones in terms of the cross-sectional area of the pipe, the hydro-dynamical " conductance " of the communicating passage c, and the natural frequencies of the pipe and Helmholtz resonators.   The method of investigation follows Rayleigh's treatment of the theory of resonance in pipes and other cavities.[*]

Let l be the length of the pipe resonator and a the " end correction," so that in the absence of the Helmholtz resonator the pipe would respond to wave-lengths given by

$$\tfrac{1}{4}\,(m\lambda) = l + a = l'\,(m = 1,\, 3,\, 5,\, \text{etc.}).$$

If the pipe is circular in section a is approximately 0·8 of the radius.   In what follows we shall confine our attention to the case when $m = 1$.   Thus the fundamental note of the pipe is

$$n_1 = \lambda_1/a = 4l'/a \tag{1}$$

where a is the velocity of sound.

Let Q be the volume of the Helmholtz resonator and c the " conductance " of the neck, then the number of vibrations per second in the fundamental resonance pitch is given by Rayleigh's formula

$$n_2 = (a/2\pi)\,\sqrt{(c/Q)}. \tag{2}$$

Let the mouth of the pipe lie in the plane $x = 0$ (fig. 1), and the axis of the pipe be parallel to the axis of x.   Then, if dissipation is left out of account,

* 'Theory of Sound,' vol. 2, Chap. XVI.

the velocity-potential inside the pipe may be written (as in the usual approximate theory of resonance in pipes),

$$\phi = \sin k\,(x-\alpha)\,\epsilon^{\iota\omega t}, \tag{3}$$

where $k = \omega/\alpha$.

Near the stopped end of the pipe the motion must ultimately depart from the plane form represented by (3). Let $-L$ be the greatest (negative) value of x for which the motion is still plane, and let ϕ_{-L} be the value of ϕ when $x = -L$. In the region, small compared with the wave-length, between the plane section of the pipe at $x = -L$ and the interior of the Helmholtz resonator, the motion will be approximately that of an incompressible fluid. Thus, if dq/dt is the rate of transfer of fluid from the pipe into the Helmholtz resonator, we have, equating the flux through the pipe at $x = -L$ to the flux in the neck,

$$\sigma\,(\partial\phi/\partial x)_{x=-L} = dq/dt \tag{4}$$

where σ is the cross-sectional area of the pipe. Also, if ψ is the velocity-potential inside the Helmholtz resonator, we have

$$dq/dt = c\,(\phi_{-L}-\psi) \tag{5}$$

and

$$\psi = \frac{a^2}{Q}\int q\,dt \tag{6}$$

so that the equation of motion of the air in the neck is—

$$\frac{d^2q}{dt^2} + \omega_2{}^2 q = c\,\frac{d\phi_{-L}}{dt}, \tag{7}$$

where $\omega_2 = 2\pi n_2$. The equation to determine the resonance frequencies is obtained by elimination of q between (4) and (7). Thus, since dq/dt and ϕ_{-L} both vary as $\epsilon^{\iota\omega t}$, we obtain

$$\left(1-\frac{\omega_2{}^2}{\omega^2}\right)\frac{dq}{dt} = c\phi_{-L}. \tag{8}$$

From (3)

$$\phi_{-L} = -\sin kL'\,.\,\epsilon^{\iota\omega t}, \tag{9}$$

where $L' = L + \alpha$. Also

$$(\partial\phi/\partial x)_{x=-L} = k\cos kL'\,.\,\epsilon^{\iota\omega t}, \tag{10}$$

whence from (7)

$$dq/dt = \sigma k\cos kL'\,.\,\epsilon^{\iota\omega t}. \tag{11}$$

By substitution from (9) and (11) in (8), the equation to determine the resonant tones is found to be.

$$\sigma k\left(1-\frac{\omega_2{}^2}{\omega^2}\right)\cos kL' = -c\sin kL',$$

or

$$\tan kL' = -\frac{\sigma k}{c}\left(1-\frac{\omega_2{}^2}{\omega^2}\right). \tag{12}$$

For comparison with experiment it is convenient to replace k, ω, and ω_2, by their equivalents in terms of n and n_2, the vibrations per second in the respective notes. Also the length L′ may be replaced by l', the " reduced length " of the pipe.

Since $k = \omega/a = 2\pi n/a$, and $l' = \frac{1}{4}\lambda_1 = a/4n_1$, equation (12) becomes

$$\tan \frac{\pi n}{2n_1} = -\frac{2\pi\sigma}{ac} n \left(1 - \frac{n_2{}^2}{n^2}\right). \qquad (13)$$

The vibrations per second in the resonant tones are given by the roots of (13), and are most conveniently found by a graphical method. For this purpose it is only necessary to plot the curves given by

$$y = \tan (\pi n/2n_1) \qquad (14)$$

and

$$y = -\frac{2\pi\sigma}{ac} n \left(1 - \frac{n_2{}^2}{n^2}\right). \qquad (15)$$

An example is given in § 4.

§ 3. *Experimental Method.*—By means of the hot‑wire microphone, equation (13) can easily be tested experimentally. In the experiment about to be described, the outer (pipe) resonator was made from two glazed earthenware pipes,* each of length 60 cm. and internal diameter 15 cm. These were cemented together to make one pipe 120 cm. long. A wooden " plunger " was fixed into this pipe at a distance of 104 cm. from one end. The plunger consisted of a wooden disc (P, fig. 2), 2·5 cm. thick and 14 cm. in diameter, from the middle of which was cut a circular hole 9 cm. in diameter. On the under surface of the wood was screwed a disc of brass (B) about 12 cm. in diameter. This brass disc carried at its centre a nipple (N) which was internally threaded, and into which the neck of the Helmholtz resonator was screwed, as shown in fig. 2. Between the brass plate and the wood was placed a washer of sheet rubber (R), which overlapped the wood and ensured a tight fit when the plunger was pushed into the pipe. The Helmholtz resonator consisted of a container (Q, fig. 2), made from brass tubing (internal diameter 5·4 cm.), into which was fitted a wooden piston (W), so that the volume, and therefore note, could be varied over a considerable range.

The microphone grid (M), and its holder, were of the same pattern as those used in previous experiments, and both are fully described in a paper to which reference has already been made.† The method of plotting resonance curves is also described in the same paper, and it is unnecessary to give more than a

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* These pipes were used as a matter of convenience. A rectangular wooden box, open at one end, gives equally good results.

† Tucker and Paris, *loc. cit.*, pp. 391–393.

brief summary here. All observations were made out-of-doors, the resonator being placed at a distance of about 2 metres from the source of sound and supported on three wooden feet, so that the pipe stood vertically with the open end downwards and about 30 cm. above the ground. The microphone grid formed one arm of a Wheatstone bridge, and the deflections of the galvanometer (a microammeter with suitable series and shunt resistances) were used to measure the response of the resonator. The microphone grids carried a maximum heating current of 28 milliampères, and had a "hot" resistance of 350 ohms.

The source of sound was a siren of the Seebeck pattern, consisting of a brass siren disc mounted on the shaft of an electric motor. The disc was pierced with a ring of 15 holes, each 1·25 cm. in diameter, and spaced so that the distance from the centre of one hole to the centre of the next (measured along the circumference of the circle on which the centres of the holes lie), was 2·5 cm. The blast of air was supplied from a gas-compressor, the delivery pipe at the siren having the same

Fig. 2.

diameter as the holes in the disc. It has been shown by Milne and Fowler[*] that when the holes are spaced in this manner (that is, when the distance from centre to centre is twice the diameter of a hole), the purity of the note given by the Seebeck siren is comparable with that of the "pure tone siren" designed by these authors. Some preliminary experiments showed that the theoretical conclusions are well borne out in practice, there being but little difference in quality between the tone of the Seebeck siren described above, and that of a 12-hole "pure tone siren" constructed as shown in Milne and Fowler's fig. 5.

The speed of the motor, which could be regulated over a wide range by means of rheostats, was recorded by an Elliott speed-counter connected with the motor by flexible shafting.

§ 4. *Graphical Solution. Comparison of Calculated and Observed Frequencies.* —In order to calculate the resonant frequencies of the double resonator, it is necessary to know the values of n_1, n_2, σ and c. To find n_1, a pair of
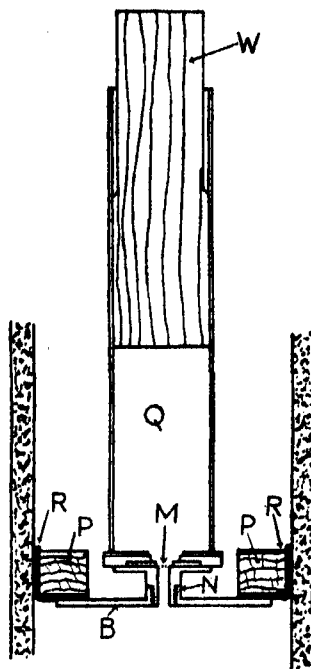
* 'Roy. Soc. Proc.,' A, vol. 98, pp. 414–427 (1921).

stethoscopes were connected by rubber tubing to the nipple N (fig. 2), and the speed of the siren necessary to give maximum resonance was determined by listening.

It was found that n_1 was 78 vibrations per second at 19° C. From this the curve corresponding to equation (14), viz.,

$$y = \tan (\pi n / 2n_1)$$

can be plotted, as in fig. 3.

The frequency n_2 of the Helmholtz resonator could be raised or lowered by
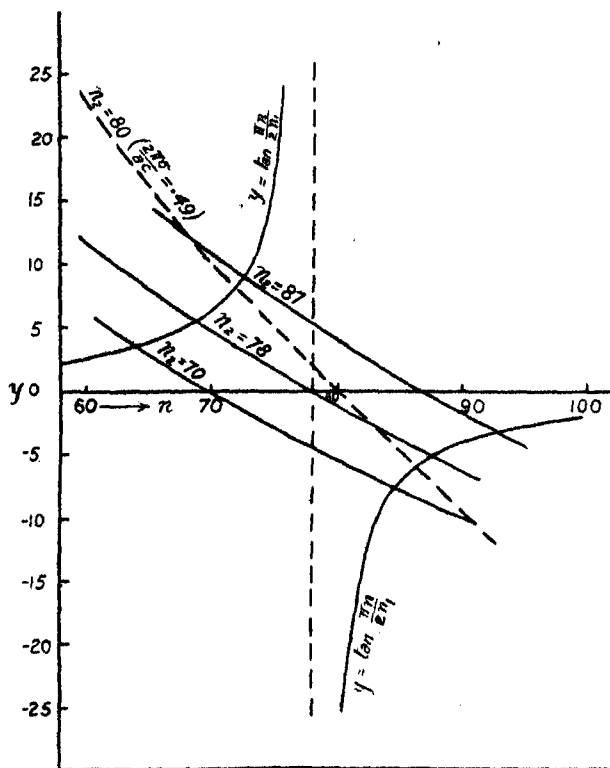
Fig. 3.

moving the wooden piston W (fig. 2). In a preliminary experiment the frequency of the resonator corresponding to various positions of W was determined, and a scale of frequencies marked on it. The range of the scale was from 63 to 87 vibrations per second.

During this preliminary experiment the Helmholtz resonator was removed from the pipe and a brass flange similar to the plate B (fig. 2) screwed on to the neck, so that the conductance had the same value as when the resonator was in position.

Since the pipe was 15·2 cm. in diameter, we have

$$\sigma = 182 \text{ cms}^2.$$

To find c the microphone holder (with the flanged neck) was fitted to a container of known volume and the pitch determined experimentally. The value of c was then calculated from the formula (2) of § 2. The value found was 0·117 cm. From these values of σ and c, we get

$$2\pi\sigma/ac = 0.286,$$

where a is the velocity of sound in air at 19° C. (the temperature at which the experiments were performed). So that (15) becomes

$$y = -0.286n\left(1 - \frac{n_2^2}{n^2}\right).$$

For comparison with the experimental results, the values 70, 78 and 87, were given to n_2 and the corresponding curves plotted as in fig. 3. The resonance frequencies of the double resonator are easily read off from the figure.

The experimental resonance curves (fig. 4) were obtained in the manner already described. Readings of the galvanometer deflection and the speed of the siren motor were taken as nearly as possible simultaneously. In fig. 4 the deflections are plotted against the siren note for six different values of n_2. When the maximum deflection occurred between two readings of the speed counter, it is indicated by a short horizontal line in the figure.

A comparison of figs. 3 and 4 shows that there is very good agreement
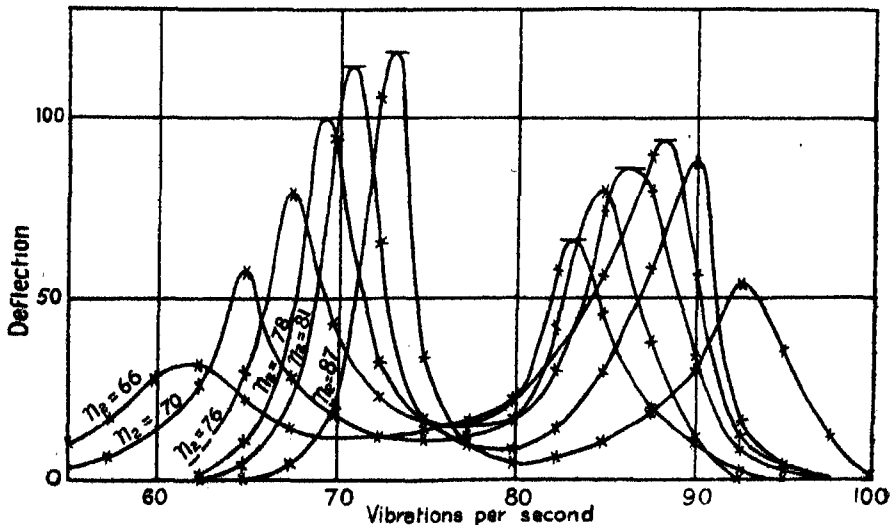
Fig. 4.

between the observed and calculated resonance frequencies. Some values of N_1 and N_2 taken from fig. 3 with the corresponding values as found by experiment, are given in the following Table :—

Table I.

n_2.	Calculated.		Observed.	
	N_1.	N_2.	N_1.	N_2.
70	84¼	64	85	65
78	87½	69	88	69
87	93	73	93	73

§ 5. *The Tuning of the Component Resonators.*—The double resonator shows the usual characteristics of a coupled system, the components of which have the frequencies n_1 and n_2. Thus, if the pitch of the pipe is kept constant while the pitch of the Helmholtz resonator is slowly raised (by reducing the volume Q) from some value well below n_1, then, whatever the value of n_2, the two resonant tones are such that the lower one (N_2) is always below both n_1 and n_2, while the upper one (N_1) is always above them. There is one value of n_2 which make the difference $N_1 - N_2$ a minimum. Let $2\pi\sigma/ac$ be fixed, so that the question is solely one of tuning the component resonators. If N_1 and N_2 were determined by the intersection of a straight line such as

$$y = \text{constant} \times (n - n_2)$$

with a tangent curve, the difference between N_1 and N_2 would be a minimum when $n_2 = n_1$. Now, in the region with which we are concerned, the curve corresponding to equation (15) does not depart very greatly from a straight line. In fact (15) may be written

$$y = -\frac{2\pi\sigma}{ac}\frac{n+n_2}{n}(n-n_2)$$

$$= -\frac{4\pi\sigma}{ac}(n-n_2) \tag{16}$$

approximately, so that the condition for N_1 and N_2 to be nearest together is $n_2 = n_1$. This conclusion is confirmed by the result of the experiment already described. It was found that the minimum difference between N_1 and N_2 was 18¾ vibrations per second and occurred when n_2 was between 77 and 78. The minimum *interval* N_1/N_2, however, occurred when n_2 was above 78.

It may also be noted that the tilt of the curve (16) is given by the factor $4\pi\sigma/ac$, and for a given value of n_2 it is this factor that determines the coupling of the system and the relative positions of N_1 and N_2. If it is large

N_1 and N_2 are close together, while if it is small they are far apart. To illustrate this point, the results of a second experiment may be quoted, in which the pipe resonator had an internal diameter of 23 cm. and the conductance of the neck joining the two resonators was 0·153 cm. This gave, at the temperature of the experiment

$$2\pi\sigma/ac = 0·491$$

instead of 0·286 as in the first experiment. The length of the pipe resonator was 100·3 cm., and it responded to a note of 79 vibrations per second. The effect of the increased ratio σ/c on the curve corresponding to (15) is shown by the broken line in fig. 3 which is worked out for the case when $n_2 = 80$. The intersection with the tangent curve gives

$$N_1 = 86\tfrac{1}{2} \text{ vibrations per second.}$$
$$N_2 = 72 \qquad \text{,,} \qquad \text{,,}$$

while the observed values were

$$N_1 = 86\tfrac{1}{4} \text{ vibrations per second.}$$
$$N_2 = 73\tfrac{1}{2} \qquad \text{,,} \qquad \text{,,}$$

The calculated values should be rather low since the tangent curve is plotted for $n_1 = 78$ instead of 79, so that the close agreement between observed and calculated values is to some extent fortuitous.

Further observations showed that the minimum difference $N_1 - N_2$ was 13 vibrations per second and the minimum interval N_1/N_2 was 1·18. Both these minima occurred when n_2 was between 77 and 80, but their positions were not determined more exactly than this.

§ 6. *The Form of the Resonance Curves.*—Fig. 4 shows how the form of the resonance curves varies with the tuning of the component resonators. Let D_1 and D_2 represent the deflection of the galvanometer (approximately proportional to the energy of the vibration) when $n = N_1$, $n = N_2$ respectively. Both D_1 and D_2 varied in a well defined manner when (n_1 being constant) the pitch n_2 of the inner resonator is changed by altering its volume. When n_2 was either far above or far below n_1, D_1 and D_2 were relatively small, but passed through maximum values when n_2 was near to n_1. The growth of D_1 is clearly shown, a maximum occurring when $n_2 = 87$ The readings, however, do not extend far enough to show the passage of D_2 through a maximum, but it occurred approximately when n_2 was 87. It was also found that D_1 and D_2 were equal when n_2 was about 77, and that, as far as the experiment showed, D_1 was always greater or less than D_2 according as n_2 was less than or greater than 77.

In the second experiment, in which a pipe 23 cm. in diameter was used

($n_1 = 79$, $2\pi\sigma/ac = 0\cdot491$), the resonance curves had the same general character. The maximum value of D_1 occurred when n_2 was 73, and of D_2 when $n_2 = 89$, while D_1 and D_2 were equal when n_2 was 79.

The application of the foregoing results to the construction of a doubly-resonated microphone which will respond to a given range of frequencies presents no difficulty. The response will necessarily be unequal since—unless the damping is very large—the resonance curve will always show two maxima. In order to reduce the inequality to a minimum, the component resonators should be tuned so that $D_1 = D_2$. The minimum deflection occurring between $n = N_1$ and $n = N_2$ then depends only on the damping and on the ratio σ/c. For example, a microphone was constructed to respond to notes between 67 and 84 vibrations per second. The outer resonator was 23 cm. in diameter and responded to a note of 74 vibrations per second. The conductance of the neck joining the two resonators was $0\cdot13$ cm., so that $2\pi\sigma/ac$ was $0\cdot59$. When the inner resonator was tuned to 73 vibrations per second, the resonance curve showed two equal maxima at 70 and 82, while at no point between 67 and 84 was the deflection less than 40 per cent. of the maximum value.

§ 7. *Theory of the Helmholtz Double Resonator.*—This type of double resonator is shown diagrammatically in fig. 5. It consists of a Helmholtz

Fig. 5.

resonator (c_1, Q_1) to which is attached a second Helmholtz resonator (c_2, Q_2) so that Q_1 and Q_2 communicate through c_2 while Q_1 communicates with the outside air through c_1. The whole resonator is supposed to be small compared with the wave-lengths of the notes to which it resounds. When a double resonator is used to obtain increased sensitivity to a particular tone, the Helmholtz double resonator is generally preferable to one of the Boys pattern.

The theory of such resonators has been given by Rayleigh,[*] who obtained, by Lagrange's method, an expression from which the natural pitches can be calculated if c_1, c_2, Q_1, and Q_2 are known.[†] Alternatively, the same result may be obtained as follows:—

Let ϕ, ψ_1, and ψ_2 represent the velocity-potentials outside the resonator, inside Q_1 and inside Q_2 respectively. Then, if q_1 denotes the transfer of fluid

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[*] 'Theory of Sound,' vol. 2, p. 190; 'Phil. Trans.,' A, vol. 161, pp. 77–118 (1870); 'Phil. Mag.,' vol. 36, pp. 231–234 (1918); 'Scientific Papers,' vol. 1, Art. 5, and vol. 6, Art. 432.

[†] More exactly, it is only necessary to know the ratios c_1/Q_1, c_2/Q_2, and c_1/c_2 or Q_1/Q_2.

through c_1 into Q_1, and q_2 denotes the transfer through c_2 from Q_1 to Q_2, we have

$$\frac{dq_1}{dt} = c_1 (\phi - \psi_1), \qquad \frac{dq_2}{dt} = c_2 (\psi_1 - \psi_2), \tag{17}$$

$$\psi_1 = a^2 \int \frac{q_1 - q_2}{Q_1} dt, \qquad \psi_2 = a^2 \int \frac{q_2}{Q_2} dt, \tag{18}$$

where a is the velocity of sound in the gas in the apertures c_1 and c_2. The equations of motion, obtained by elimination of ψ_1 and ψ_2 from (17) and (18) are

$$\left. \begin{aligned} \frac{d^2 q_1}{dt^2} + \frac{a^2 c_1}{Q_1} (q_1 - q_2) &= c_1 \frac{d\phi}{dt} \\ \frac{d^2 q_2}{dt^2} + a^2 c_2 \left(\frac{q_2}{Q_2} - \frac{q_1 - q_2}{Q_1} \right) &= 0 \end{aligned} \right\}. \tag{19}$$

To find the natural tones (without allowance for dissipation) let $d\phi/dt = 0$, and assume that q_1 and q_2 both vary as $\epsilon^{i\omega t}$. We thus obtain

$$\omega^4 - a^2 \omega^2 \left(\frac{c_1 + c_2}{Q_1} + \frac{c_2}{Q_2} \right) + a^4 \frac{c_1 c_2}{Q_1 Q_2} = 0, \tag{20}$$

which is the equation given by Rayleigh.[*]

This result may be shown in a more convenient form.

Let $\quad c_2 = \mu c_1, \quad \omega = 2\pi n, \quad n_1^2 = a^2 c_1 / 4\pi^2 Q_1, \quad$ and $\quad n_2^2 = a^2 c_2 / 4\pi^2 Q_2$. Then (20) may be written

$$n^4 - n^2 \{ (\mu + 1) n_1^2 + n_2^2 \} + n_1^2 n_2^2 = 0. \tag{21}[\dagger]$$

It is also convenient to write $n_\mu^2 = n_2^2 + \mu n_1^2$, and it is easily seen that n_μ is the natural frequency of q_2 when $c_1 = 0$; that is, when all communication with the outer air is suppressed. If N_1^2 and N_2^2 are the roots of (21) regarded as a quadratic in n^2, we have

$$\left. \begin{aligned} N_1^2 \\ N_2^2 \end{aligned} \right\} = \tfrac{1}{2} (n_1^2 + n_\mu^2) \pm \tfrac{1}{2} \{ (n_1^2 + n_\mu^2)^2 - 4 n_1^2 n_2^2 \}^{\frac{1}{2}}. \tag{22}$$

Equation (22) allows us to calculate the frequencies of the resonant tones for given values of μ, n_1, and n_2. There is, however, a graphical method of finding N_1 and N_2 which is worth attention on account of the analogy with the case of the Boys resonator. Equation (21) may be written

$$\frac{n}{1 - (n^2 / n_1^2)} = -\frac{c_1}{c_2} n \left(1 - \frac{n_2^2}{n^2} \right). \tag{23}$$

A comparison with equation (13) of § 2 shows that both (13) and (23) have the form

$$f(n, n_1) = -K n (1 - (n_2^2 / n^2)).$$

[*] 'Theory of Sound,' vol. 2, p. 191 (Equation (12)).

[†] Rayleigh, 'Sci. Papers,' vol. 6, p. 550.

For the Boys resonator,

$$\left.\begin{array}{l} f\,(n,\ n_1) = \tan\,(\pi n/2n_1) \\ K = 2\pi\sigma/ac \end{array}\right\} . \tag{24}$$

While (23) shows that for the double Helmholtz resonator

$$\left.\begin{array}{l} f\,(n,\ n_1) = \dfrac{n}{1-(n^2/n_1^2)} \\ K = c_1/c_2 \end{array}\right\} . \tag{25}$$

In both cases the value of y changes from positive to negative infinity as n passes through the value n_1. When n_1 and n_2 are given, the coupling and relative position of the resonant tones is determined by the parameter K. If K is large, N_1 and N_2 will be close together, whereas if it is small they will be far apart.

The actual values of N_1 and N_2 in the Helmholtz double resonator can be determined graphically by finding the intersections of the curves

$$y = \frac{n}{1-(n^2/n_1^2)} \tag{26}$$

and

$$y = -\frac{c_1}{c_2}\,n\,(1-(n_2^2/n^2)). \tag{27}$$

It may be observed that the equations of motion (19) are of the usual type for undamped force-coupled systems with two degrees of freedom. They may be written[*]

$$\left.\begin{array}{l} \dfrac{d^2 q_1}{dt^2} + \omega_1^2 q_1 + \gamma_1 \omega_1^2 q_2 = c_1\,\dfrac{d\phi}{dt} \\[2mm] \dfrac{d^2 q_2}{dt^2} + \omega_\mu^2 q_2 + \gamma_2 \omega_\mu^2 q_1 = 0 \end{array}\right\} , \tag{28}$$

where $\gamma_1 = -1,\qquad \gamma_2 = -\mu\omega_1^2/\omega_\mu^2 = -\mu n_1^2/n_\mu^2.$

The coefficient of coupling is $\sqrt{(\gamma_1\gamma_2)}$ or $(n_1/n_\mu)\sqrt{\mu}$. The analogous electrical circuit consists of two inductances (L_1 and L_2) and two capacities (C_1 and C_2)
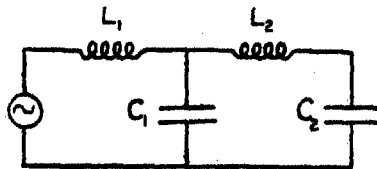
Fig.6.

coupled, as shown in fig. 6. In this analogy the electrical inductances correspond to the *reciprocals* of the hydrodynamical "conductances" in the

[*] *Cf.* M. Wien, ‘Annalen der Physik,’ vol. 61, p. 155 (1897).

acoustical circuit, while the electrical capacities correspond to the volumes of the acoustical resonators.* The coefficient of coupling in the electrical circuit is $\sqrt{\{C_2/(C_1+C_2)\}}$, whence, by analogy, the corresponding quantity in the acoustical circuit is $\sqrt{\{Q_2/(Q_1+Q_2)\}}$ or $(n_1/n_\mu)\sqrt{\mu}$.

§ 8. *Graphical Solution. Comparison with Experiments.*—The following experiment illustrates the formulæ of the preceding section. The general procedure was the same as that given in § 3. The outer resonator (c_1, Q_1) was made from a pipe 23 cm. in diameter (internal),† at one end of which was fixed a disc of wood, 2·5 cm. thick, and with a circular hole, 6·4 cm. in diameter, cut from the centre. A "plunger," similar to that shown in fig. 2 and carrying a Helmholtz resonator (c_2, Q_2), whose volume could be varied at
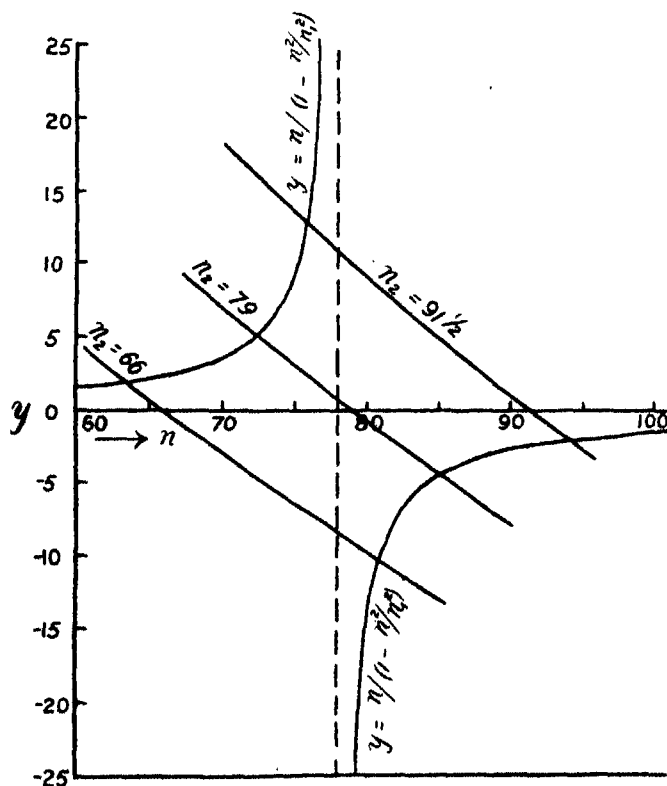
Fig. 7.

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* If the neck c_1 (fig. 5), instead of communicating with the outside air, is made to lead into a third enclosed volume, we obtain a coupled acoustical system which has been investigated by Hahnemann and Hecht, 'Physikalische Zeitschrift,' vol. 22, p. 357 (1921). An electrical analogue is described which is of a similar kind to that given above for the Helmholtz double resonator.

† A rectangular wooden box serves equally well.

will, was placed in the pipe at a distance of 49·5 cm. from the wooden disc. The microphone grid and its holder were of the same pattern as in the first experiment, and the pitch of the outer resonator was found to be 78 vibrations per second at 19° C. The curve corresponding to (26), with $n_1 = 78$, is plotted in fig. 7.

The conductances of the two orifices were —

$$c_1 = 4·42 \text{ cms.}, \qquad c_2 = 0·117 \text{ cm.},$$

so that $c_1/c_2 = 37·8$.

The curves corresponding to (27) were worked out in three cases and are shown in fig. 7.

The experimentally obtained resonance curves are reproduced in fig. 8. In order to show the growth of the maxima at the resonance frequencies, the
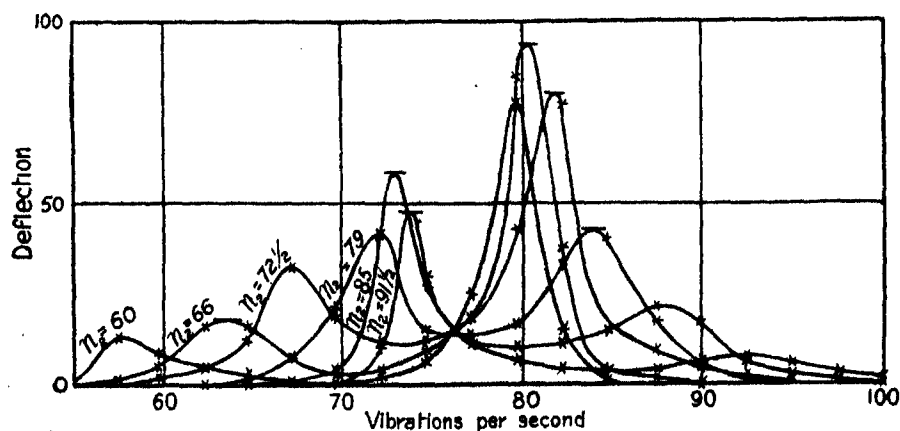
FIG. 8.

curves are given for six values of n_2, ranging from 60 to $91\frac{1}{2}$. Some observed values of N_1 and N_2, corresponding to values taken from fig. 7, are shown in the following Table.

Table II.

n_2.	Calculated.		Observed.	
	N_1.	N_2.	N_1.	N_2.
66	81	$68\frac{1}{2}$	$80\frac{1}{2}$	$68\frac{1}{2}$
79	85	72	84	72
$91\frac{1}{2}$	93	75	93	74

§ 9. *Conditions for the Difference (or Interval) between the Resonant Tones to be a Minimum.*—The general behaviour of the Helmholtz double resonator

when the tuning of the components is altered, is similar to that of the Boys resonator described in § 5. The question, however, as to how the component resonators should be tuned in order to make either $N_1 - N_2$ or N_1/N_2 a minimum, can be answered more definitely than in the case of the last-named resonator. Thus the condition for $N_1 - N_2$ to be a minimum when n_2 is constant and n_1 is varied, or *vice versa*, can be found from

$$(\partial/\partial n_1, \ \partial/\partial n_2)(N_1 - N_2) = 0.$$

On substituting the appropriate values of N_1 and N_2 from (22) it is found : (i) that when n_1 is constant $(N_1 - N_2)$ is a minimum when $n_2 = n_1$; and (ii) that when n_2 is constant $(N_1 - N_2)$ is a minimum when $n_1 = n_2/(1 + \mu)$.

By putting $n_2 = n_1$ in (22) it is found that the values of N_1 and N_2 when $(N_1 - N_2)$ is a minimum, n_1 being constant, are

$$\left.\begin{matrix} N_1 \\ N_2 \end{matrix}\right\} = \frac{n_1}{\sqrt{2}} \{\mu + 2 \pm \sqrt{(\mu \, [\mu + 4])}\}^{\frac{1}{2}}. \tag{29}$$

The values of N_1 and N_2 in the corresponding case when n_2 is constant and n_1 is varied, can be obtained from (29) by writing $n_2/\sqrt{(1 + \mu)}$ in place of n_1.

These results can be confirmed by reference to the experiment already described. In this experiment

$$n_1 = \text{constant} = 78,$$

$$\mu = 1/37\cdot 8 = 0\cdot 0265.$$

According to the above, $(N_1 - N_2)$ should therefore be a minimum when n_2 is 78, and the value of this minimum should be $84\cdot 6 - 71\cdot 9 = 12\cdot 7$. The values found in the experiment were $78\cdot 5$ and 12.

If μ is given, the interval N_1/N_2 is a function of the interval n_1/n_2 only. Let $p = n_2/n_1$. Then for N_1/N_2 to be a minimum we must have

$$(d/dp)(N_1/N_2) = 0,$$

from which, by means of (22), it is found that the required condition is

$$p = n_2/n_1 = \sqrt{(1 + \mu)}. \tag{30}$$

From (30) and (22) it appears that the minimum value of N_1/N_2 is

$$\left[\frac{N_1}{N_2}\right] = \left\{\frac{\mu + 1 + \sqrt{(\mu \, [\mu + 1])}}{\mu + 1 - \sqrt{(\mu \, [\mu + 1])}}\right\}^{\frac{1}{2}}. \tag{31}$$

If $n_1 = 78$ and $\mu = 0\cdot 0265$, as in the experiment described above, it is found from (30) and (31) that

$$n_2 = 79, \qquad [N_1 - N_2] = 1\cdot 18.$$

The values found by experiment were 79 and $1\cdot 17$.

§ 10. *Form of the Resonance Curves and Sensitivity.*—The form of the resonance

curves depends on the coupling (measured by $(n_1/n_\mu)\sqrt{\mu}$), and damping of the component resonators.   In the case of the singly resonated microphone, the dissipation of energy can be represented in the equation of motion by a term proportional to the instantaneous current of air in the neck of the resonator.[*] Similarly, the dissipation of energy in the double resonator can be represented by terms proportional to the currents in the apertures c_1 and c_2.   When these terms are introduced, the equations of motion become

$$\left.\begin{array}{l}\dfrac{d^2q_1}{dt^2}+2h_1\dfrac{dq_1}{dt}+\omega_1{}^2q_1-\omega_1{}^2q_2=\dfrac{c_1\mathrm{F}}{\rho}\,\epsilon^{i\omega t}\\[2ex]\dfrac{d^2q_2}{dt^2}+2h_2\dfrac{dq_2}{dt}+\omega_\mu{}^2q_2-\mu\omega_1{}^2q_1=0\end{array}\right\},\qquad(32)$$

where F is the pressure amplitude due to the source (supposing the mouth of the resonator to be closed), ρ is the density of the air, and h_1 and h_2 are due to the operation of viscous forces in the apertures c_1 and c_2, and to the escape of acoustical energy into the surrounding air.   The proportions in which these causes contribute to h_1 and h_2 depend on the exact size and shape of the apertures concerned, but whatever they may be, h_1 and h_2 will be functions of the frequency of the vibrations.

The equations (32) have the usual well-known solutions.[†]   In the present case we are concerned only with the energy of the forced vibration in the second aperture, which is proportional to $\left|\dfrac{dq_2}{dt}\right|^2$, and it is easily shown from (32) that

$$\left|\frac{dq_2}{dt}\right|^2=\frac{\omega^2\omega_1{}^4\,c_2{}^2\mathrm{F}^2/\rho}{\left[\{(\omega_1{}^2-\omega^2)(\omega_\mu{}^2-\omega^2)-\mu\omega_1{}^4-4h_1h_2\omega^2\}^2\right.}.\qquad(33)$$
$$\left.+4\omega^2\{h_1(\omega_\mu{}^2-\omega^2)+h_2(\omega_1{}^2-\omega^2)\}^2\right]$$

Approximate numerical values for h_1 and h_2 can be found by assuming that they are constant for the range of frequencies contained in the resonance curve.   Thus h_2 can be found by plotting the resonance curve of the inner resonator by itself, and when h_2 is known, an approximate value for h_1 can be obtained from (33), by finding what value will produce the best agreement between the observed and calculated resonance curves.   For example, in the experiment described in §8, it was found in this way that approximate values were $h_1 = 4$ and $h_2 = 20$.

It has previously been pointed out,[‡] that in narrow apertures (such as c_2 in the foregoing experiment) the dissipation due to the diffusion of acoustical energy into the surrounding air contributes only a negligibly small amount

* Tucker and Paris, *loc. cit.*, pp. 398–399.
† See M. Wien, *loc. cit.*, p. 181.
‡ Tucker and Paris, *loc. cit.*, p. 399.

to the damping factor. The case of a wide aperture, such as c_1, however, is somewhat different. This aperture had a diameter of 6·4 cm., and a conductance of 4·4 cm. The damping factor, if viscosity were left out of account, would be $\omega^2 c / 2\pi a$ (supposing the opening to be flanged), or 2·3 if $\omega/2\pi = 75$ vibrations per second. Thus the escape of energy from the resonator accounts for more than half of the experimentally determined value of h_1.

By making use of these approximate values of h_1 and h_2, it can be shown from (33) that a doubly-resonated microphone of the type described may be more than one hundred times as sensitive (to one of its resonant tones) as a suitably tuned singly-resonated microphone with an aperture similar to that of the inner resonator. This remarkable increase in sensitivity is in accordance with experience.

It was pointed out by Rayleigh[*] that, for great sensitivity, the inner resonator must be small compared with the outer one. In Rayleigh's investigation (which takes no account of dissipation) it is shown that if n_1 and n_2 are equal, and if Q_2 is small compared with Q_1, then the ratio of the maximum velocity in the second aperture to that in the first is given by

$$V_2/V_1 = (Q_1/Q_2)^{3/2}. \qquad (34)$$

According to this result, V_2 could be made to exceed V_1 to any extent simply by making Q_2 small enough. It is more satisfactory, however, to make use of (33), by means of which the values of V_2 can be compared under different circumstances without reference to V_1. Moreover, it is found in practice that the effect of dissipation is by no means negligible, for when Q_2 is diminished it is necessary also to reduce c_2 (the conductance of the second aperture) in order that the ratio c_2/Q_2, and hence n_2, may be maintained at its former value. This can be done either by increasing the length of the opening or by reducing its cross-sectional area. In either case, the damping factor h_2 will be increased, and this, as shown by (33), tends to neutralise the advantage gained by the reduction in Q_2. The effect of viscosity becomes important when the second aperture is made very small, and for this reason there is probably no advantage in making the cross-section (supposed circular) much less than 3 or 4 mm. in diameter.

In hot-wire microphones, the extent to which the cross-section of the second aperture can be advantageously reduced is limited by the size of the grid. The smallest openings that have been used by the author were 3 mm. in diameter (internal) and between 2 and 3 mm. long. These were used in double resonators constructed to respond to notes of 250 vibrations per second

* 'Phil. Mag.,' vol. 36, pp. 231-234 (1918) ; 'Sci. Papers,' vol. 6, pp. 549-551.

and upwards. Besides being very sensitive, these microphones had the additional advantage that the hot-wire grid was well screened from draughts and wind.

In the case of larger apertures, the increase in sensitivity obtained by a reduction of the cross-sectional area is very marked. Thus, in a certain experiment, the second aperture was merely the circular hole in the mica plate which is used to carry the grid, while the "grid" itself was a single strand of wire fastened across the opening. The inner and outer resonators were each tuned to 108 vibrations per second. In the first part of the experiment, the diameter of the aperture was 1 cm., and this was reduced in the second part to 0·5 cm. The effect of this reduction was to increase the response (measured in ohms change per centimetre of wire exposed) to five times its first value at the higher note, and three times at the lower note. Precautions were taken to ensure that the amplitude of the sound affecting the microphone was the same in each case, and that the enhanced effect was due to an increase in the acoustical, as distinct from the electrical sensitivity.

§ 11. *Summary.*—The paper records the result of investigations into the properties of double resonators which can be used with hot-wire microphones in order to increase sensitivity, and also, if desired, to widen the range of response. Two types of resonator are dealt with, namely :—

(i) The "Boys double resonator," consisting of a "stopped pipe" in series with a Helmholtz resonator. The theory is given and experiments are described which illustrate the results obtained.

(ii) The "Helmholtz double resonator," consisting of two Helmholtz resonators in series. Rayleigh's theory is extended and experiments are described, the results of which show a satisfactory agreement with the theoretical formulæ. The form of the resonance curves is discussed, and the conditions affecting the sensitivity.

§ 12. *Conclusion.*—The greater part of the work described in this paper was done at the Signals Experimental Establishment, Woolwich, and is now published by permission of the War Office.

The author is indebted to Major W. S. Tucker for much useful advice and assistance.

The Thermal Stresses in Solid and in Hollow Circular Cylinders concentrically Heated.

By Charles H. Lees, D.Sc., F.R.S.

1. The large differences of temperature which exist between the inside and outside of the heating or firing tunnels used in pottery and other works, and between the inner and outer portions of the concrete or masonry pillars supporting the floors of a building in which a fire occurs, make the thermal stresses approach the breaking strength of the materials and they are crushed or torn asunder. The same may be said to a less degree of chimney stacks, and of the walls of the cylinders of internal combustion engines.

In order to prevent this, it is necessary to design the structure so as to withstand the stresses which will be produced by the differences of temperature to which they will be subjected. The calculation of these stresses has only been carried out for a hollow cylinder of constant elasticity and heat conductivity, with the temperature throughout it following the steady logarithmic law and the material expanding according to the linear law.[*]

It is proposed to treat the problem in a more general way in the present communication, and to show that for any temperature distribution, with any law of expansion, the stresses may be found by a simple graphical method so long as the variation of the elastic constants with temperature may be neglected.

Determination of the Stresses.

2. Let a hollow circular cylinder, of internal radius r_1 and external radius r_2, and considerable length, originally at constant temperature, and not subjected to any pressure, have its temperature raised so that the temperature of each point of a cylindrical surface of radius r within it is raised to θ, where θ is a function of r. Let the cylinder then be subjected to a uniform pressure, R_1, at its inner, a uniform pressure, R_2, at its outer curved surface, and a uniform pressure, X, at each of its end surfaces. To find the mechanical and thermal stresses at each point of the material of the cylinder.
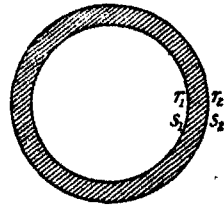
Fig. 1.—Radii, r_1 and r_2; sectional areas, s_1 and s_2.

In the first instance we note that a uniform rise of temperature would produce a uniform expansion of the cylinder, and no stresses would result

* See R. Lorenz, 'Zeitsch. Verein Deutsch. Ing.,' vol. 51, p. 743 (1907).

from such an expansion. We therefore divide the final temperature, θ, into two parts: first, a uniform temperature, $\bar{\theta}$, to which the cylinder would have to be heated to give the same expansion of the whole shell as that produced by the actual temperature, θ; second, the excess, θ', of the actual temperature over this uniform temperature.

Thus
$$\theta = \bar{\theta} + \theta'.$$

Whatever the character of the law of expansion of the material of the shell with rise of temperature, we may write $v_\theta = v_0(1 + \alpha_\theta)$ where v_0 is the volume of an element at $0°$ C. and v_θ at $\theta°$ C., and α_θ is the increase of volume of 1 c.c. when raised from $0°$ C. to $\theta°$ C. Hence if $\bar{\alpha}$ is the mean expansion for the whole shell and α_θ' the excess at a point where the temperature is θ over the mean expansion, we have $\alpha_\theta = \bar{\alpha} + \alpha_\theta'$.

Next we notice that, although the pressures on the end surfaces are uniform the pressures in planes parallel to them cease to be uniform, owing to the variation of θ' with r. In planes at distances from the end surfaces greater than the thickness of the cylinder these pressures become independent of the positions of the planes.

In the middle length of the cylinder points initially in a plane perpendicular to the axis of the cylinder at x are still in a plane perpendicular to the axis and at $x + x'$ after the expansion, and the initial distance, dx, apart of two such planes becomes $(1 + (dx'/dx)\,dx$ after expansion, and is independent of r. The same statement would hold for the whole length of the cylinder, provided the end surfaces were kept plane by pressures or tractions applied in a suitable way over them.

Under these circumstances the only stresses acting on an elementary portion of the material bounded by two planes perpendicular to the axis at distance x and $x + dx$ from some fixed plane, by two cylindrical surfaces of radii r and $r + dr$, and two planes through the axis making angles ϕ and $\phi + d\phi$ with some fixed axial plane, are the equal axial pressures, X, acting on the surfaces perpendicular to the axis, the radial pressures, R and R + dR, on the
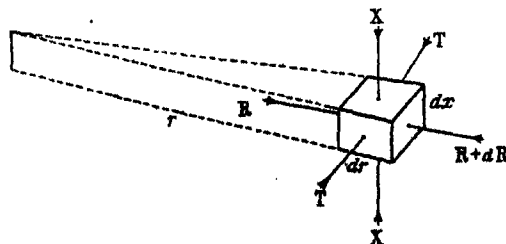
Fig. 2.—The pressures—R, radial; T, tangential; and X, axial, at the faces of an element.

inner and outer cylindrical surfaces respectively, and the equal tangential pressures, T, acting on the axial surfaces at right angles to those surfaces (fig. 2). If the displacement outwards of a point originally r from the axis is r', the stress-strain equations for the elementary portion of the material are

$$\frac{1}{\epsilon} \left\{ -R + \sigma (T + X) \right\} = \frac{dr'}{dr} - \tfrac{1}{3} \alpha_\theta', \tag{2.1}$$

$$\frac{1}{\epsilon} \left\{ -T + \sigma (R + X) \right\} = \frac{r'}{r} - \tfrac{1}{3} \alpha_\theta', \tag{2.2}$$

$$\frac{1}{\epsilon} \left\{ -X + \sigma (R + T) \right\} = \frac{dx'}{dx} - \tfrac{1}{3} \alpha_x', \tag{2.3}$$

where ϵ is Young's modulus, σ Poisson's ratio for the material, and dx'/dx is independent of r and x and may be written α_x.

The stress equilibrium equation is

$$T = R + r \frac{dR}{dr}, \tag{2.4}$$

Multiplying (2.3) through by σ and adding to (2.2) we get

$$\frac{1}{\epsilon} \left\{ -T + \sigma R + \sigma^2 (R + T) \right\} = \frac{r'}{r} + \sigma \alpha_x - \frac{1 + \sigma}{3} \cdot \alpha_\theta'. \tag{2.5}$$

Subtracting (2.2) from (2.1) we get

$$\frac{1 + \sigma}{\epsilon} (T - R) = \frac{dr'}{dr} - \frac{r'}{r}.$$

Substituting for $T - R$ from (2.4) this gives

$$\frac{1 + \sigma}{\epsilon} \frac{dR}{dr} = \frac{d}{dr} \left(\frac{r'}{r} \right) \tag{2.6}$$

and

$$\frac{1 + \sigma}{\epsilon} R = \frac{r'}{r} + \text{a constant.}$$

Differentiating (2.5) with respect to r, assuming that the variations of ϵ and σ with the radius are negligible and subtracting the result from (2.6) we get

$$\frac{1 - \sigma^2}{\epsilon} \frac{d}{dr} (T + R) = \frac{1 + \sigma}{3} \frac{d\alpha_\theta'}{dr}.$$

Integrating this gives us

$$T + R = \frac{1}{3} \frac{\epsilon}{1 - \sigma} \alpha_\theta' + A', \tag{2.7}$$

where A' is a constant of integration.

Substituting for T from (2.4) we get

$$2R + r \frac{dR}{dr} = \frac{1}{3} \frac{\epsilon}{1 - \sigma} \alpha_\theta' + A'.$$

Multiplying through by r and integrating we have

$$r^2 \mathrm{R} = \mathrm{B}' + \mathrm{A}' \frac{r^2}{2} + \frac{1}{3} \frac{\epsilon}{1-\sigma} \int \alpha_\theta' \cdot r\, dr.$$

The form of this equation suggests the expression of the stresses in terms of s the area of the circle of radius r instead of r. The equation becomes

$$\mathrm{R}s = \mathrm{A}s + \mathrm{B} + \frac{1}{6} \frac{\epsilon}{1-\sigma} \int^s \alpha_\lambda' \cdot ds, \tag{2.8}$$

where $\qquad \mathrm{A} = \dfrac{\pi \mathrm{A}'}{2} \qquad$ and $\qquad \mathrm{B} = \pi \mathrm{B}'.$

Hence R_1 and R_2, the pressures on the inside and outside surfaces respectively, satisfy the equations

$$\mathrm{R}_1 s_1 = \mathrm{A}s_1 + \mathrm{B} + \frac{1}{6} \frac{\epsilon}{1-\sigma} \int^{s_1} \alpha_\theta'\, ds,$$

$$\mathrm{R}_2 s_2 = \mathrm{A}s_2 + \mathrm{B} + \frac{1}{6} \frac{\epsilon}{1-\sigma} \int^{s_2} \alpha_\theta'\, ds.$$

Hence $\qquad \mathrm{R}s - \mathrm{R}_1 s_1 = \mathrm{A}(s - s_1) + \dfrac{1}{6} \dfrac{\epsilon}{1-\sigma} \cdot \displaystyle\int_{s_1}^s \alpha_\theta'\, ds$

and $\qquad \mathrm{R}_2 s_2 - \mathrm{R}_1 s_1 = \mathrm{A}(s_2 - s_1) \qquad$ since $\qquad \displaystyle\int_{s_1}^{s_2} \alpha_\theta'\, ds = 0.$

On elimination of A these give

$$\mathrm{R} = \frac{\mathrm{R}_2 s_2 - \mathrm{R}_1 s_1}{s_2 - s_1} + \frac{(\mathrm{R}_1 - \mathrm{R}_2) s_1 s_2}{s_2 - s_1} \frac{1}{s} + \frac{1}{6} \frac{\epsilon}{1-\sigma} \frac{\mathrm{E}'}{s}, \tag{2.9}$$

where

$$\mathrm{E}' = \int_{s_1}^s \alpha_\theta' \cdot ds = \int_{s_1}^s (\alpha_\theta - \bar{\alpha})\, ds = \mathrm{E}_\theta - \bar{\alpha}(s - s_1) = \mathrm{E}_\theta - \mathrm{E}_2 \frac{s - s_1}{s_2 - s_1},$$

E_2 being the value of E_θ at the outer surface.

Or if u be written for $1/s$ throughout the coefficients

$$\mathrm{R} = \frac{\mathrm{R}_2 u_1 - \mathrm{R}_1 u_2}{u_1 - u_2} + \frac{\mathrm{R}_1 - \mathrm{R}_2}{u_1 - u_2} \frac{1}{s} + \frac{1}{6} \frac{\epsilon}{1-\sigma} \frac{\mathrm{E}'}{s}. \tag{2.10}$$

Equation (2.4) becomes $\mathrm{T} = \mathrm{R} + 2s \dfrac{d\mathrm{R}}{ds}$ hence

$$\mathrm{T} = \frac{\mathrm{R}_2 u_1 - \mathrm{R}_1 u_2}{u_1 - u_2} - \frac{\mathrm{R}_1 - \mathrm{R}_2}{u_1 - u_2} \frac{1}{s} + \frac{1}{6} \frac{\epsilon}{1-\sigma} \left(2\alpha_\theta' - \frac{\mathrm{E}'}{s} \right). \tag{2.11}$$

On substituting for R and T in equation (2.3) we get

$$\mathrm{X} = -\epsilon a_x + 2\sigma \frac{\mathrm{R}_2 u_1 - \mathrm{R}_1 u_2}{u_1 - u_2} + \frac{1}{6} \frac{\epsilon}{1-\sigma} 2\alpha_\theta'. \tag{2.12}$$

On substituting for R, T, and X in equation (2.2) we get

$$\frac{r'}{r} = \frac{1}{2} \cdot \frac{s'}{s} = \frac{1+\sigma}{\epsilon} \left\{ -(1-2\sigma)\frac{R_2 u_1 - R_1 u_2}{u_1 - u^2} + \frac{R_1 - R_2}{u_1 - u_2} \cdot \frac{1}{s} \right\} - \sigma a_x + \frac{1}{6}\frac{1+\sigma}{1-\sigma}\frac{E'}{s}.$$

(2.13)

The fractional increase of length a_x in the axial direction and the part X_1 of X which is independent of r and x may be given any arbitrary values so long as their sum $X_1 + \epsilon a_x$ is kept equal to $2\sigma\frac{R_2 u_1 - R_1 u_2}{u_1 - u_2}$.

Thus if the increase of length a_x is taken zero $X_1 = 2\sigma\frac{R_2 u_1 - R_1 u_2}{u_1 - u_2}$, while if

X_1 is taken zero $a_x = 2\sigma\frac{R_2 u_1 - R_1 u_2}{u_1 - u_2}$.

Whatever value is assigned to a_x it only affects the expressions for the mechanical portions of the stresses and displacements, the terms for the thermal stresses and displacements are unaffected. They depend on E' and $dE'/ds = \alpha_\theta'$ only.

The mean pressure $\frac{1}{3}(R+T+X)$ at the point r is given by

$$\frac{1}{3}(R+T+X) = \frac{2}{3}(1+\sigma)\frac{R_2 u_1 - R_1 u_2}{u_1 - u_2} - \frac{\epsilon}{3}a_x + \frac{1}{6}\frac{\epsilon}{1-\sigma}\frac{4\alpha_\theta'}{3},$$

(2.14)

the shear stress in the plane T, X is given by

$$\frac{1}{3}(X-T) = -\frac{1-2\sigma}{3}\cdot\frac{R_2 u_1 - R_1 u_2}{u_1 - u_2} + \frac{1}{3}\frac{R_1 - R_2}{u_1 - u_2}\cdot\frac{1}{s} - \frac{\epsilon}{3}a_x + \frac{1}{6}\frac{\epsilon}{1-\sigma}\cdot\frac{1}{3}\frac{E'}{s},$$

(2.15)

and in the plane R, T by

$$\frac{1}{3}(R-T) = \frac{2}{3}\frac{R_1 - R_2}{u_1 - u_2}\cdot\frac{1}{s} + \frac{1}{6}\frac{\epsilon}{1-\sigma}\left(-\frac{2}{3}\alpha_\theta' + \frac{2}{3}\frac{E'}{s}\right),$$

(2.16)

and in the plane R, X by

$$\frac{1}{3}(R-X) = \frac{1-2\sigma}{3}\cdot\frac{R_2 u_1 - R_1 u_2}{u_1 - u_2} + \frac{1}{3}\frac{R_1 - R_2}{u_1 - u_2}\cdot\frac{1}{s} + \frac{\epsilon}{3}a_x$$

$$+ \frac{1}{6}\frac{\epsilon}{1-\sigma}\left(\frac{1}{3}\frac{E'}{s} - \frac{2}{3}\alpha_\theta'\right).$$

(2.17)

The terms involving the internal and external pressures are identical with those given by Lamé in his Leçons and quoted by Love.[*]

If the cylinder is solid, the constant of integration B in equation (2.8) becomes zero. On making this change in the calculations giving the stresses it is found that the term $\frac{R_2 u_1 - R_1 u_2}{u_1 - u_2}$ in the expression for each stress reduces to R_2—the pressure on the outside surface—the term involving $R_1 - R_2$

[*] Love, 'Theory of Elasticity,' 2nd edit., p. 141 (1906).

disappears, that involving a_x remains, while the terms giving the thermal part of the stresses remain unchanged in form, but E' is now $\int_0^s a_\theta' \cdot ds$ and $\dfrac{E'}{s}$ at $s = 0$ becomes $\left(\dfrac{dE'}{ds}\right)_0$ that is a_θ' at the centre, so that the thermal radial pressure does not become zero at the centre, but the shear stress in the R, T plane does.

Graphical Constructions for the Stresses and Displacements.

3. The foregoing expressions for the stresses and displacements lead to the following methods of representing and determining both graphically.

A. *The Stresses Due to the Pressures on the Inner and Outer Surfaces.*

Set off along the axis of abscissæ, fig. 3, the reciprocals $OU_1 = u_1$ and $OU_2 = u_2$ of the areas s_1 and s_2 of the circles bounding the normal section of the cylinder. At U_2 erect the ordinate U_2R_2, equal on some convenient scale to the pressure R_2 on the outside surface. Join the end R_2 of this ordinate to the point U_1, and produce to cut the axis of pressure in S_0. Through S_0 draw a straight line parallel to the axis of abscissæ, and let it cut the ordinates through U_2 and U_1 in S_2 and S_1. Set off above S_1 a length S_1R_1, equal to R_1 the pressure on the inner surface, join the end of this ordinate to S_2, and produce to cut the axis of pressure in S_0'.

Then OS is $R_2 \cdot \dfrac{u_1}{u_1 - u_2}$, S_0S_0' is $R_1 \cdot \dfrac{u_2}{u_1 - u_2}$, hence $OS_0' = \dfrac{R_2u_1 - R_1u_2}{u_1 - u_2}$, that is the constant term in the expressions for the stresses.

To get the term involving $\dfrac{R_1 - R_2}{u_1 - u_2} u$, erect at U_1, fig. 4, the ordinate $U_1A = R_1 - R_2$, join the end of it to the point U_2 and draw through O a straight line OB parallel to this join. The ordinate US at any point U is then $= \dfrac{R_1 - R_2}{u_1 - u_2} \cdot u$.
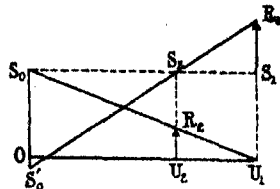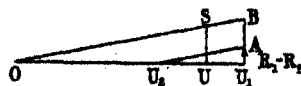
FIG. 3.   FIG. 4.

FIG. 3.—$OU_2 = u_2$, $OU_1 = u_1$, OS_0' the mean pressure (tension) determined by U_2R_2, $U_1R_2S_0$, $S_0S_2S_1$, S_1R_1 and $R_1S_2S_0$.

FIG. 4.—The variable stress US determined from $U_1A = R_1 - R_2$, U_2A and OSB.

The mechanical stresses are then given as follows :

$$R = OS_0' + US,\qquad(3.1)$$

$$T = OS_0' - US,\qquad(3.2)$$

$$X = -\epsilon a_x + 2\sigma \cdot OS_0',\qquad(3.3)$$

$$\frac{r'}{r} = \frac{1+\sigma}{\epsilon}\{-(1-2\sigma)OS_0' + US\} - \sigma a_x,\qquad(3.4)$$

the mean pressure

$$\frac{1}{3}(R+T+X) = \frac{2}{3}(1+\sigma)OS_0' - \frac{\epsilon}{3}a_x,\qquad(3.5)$$

the shear stresses

$$\frac{1}{3}(X-T) = -\frac{1-2\sigma}{3}OS_0' + \frac{1}{3}US - \frac{\epsilon}{3}a_x,\qquad(3.6)$$

$$\frac{1}{3}(R-T) = \frac{2}{3}US,\qquad(3.7)$$

and

$$\frac{1}{3}(R-X) = -\frac{1-2\sigma}{3}OS_0' - \frac{1}{3}US + \frac{\epsilon}{3}a_x.\qquad(3.8)$$

B. *Stresses Due to the Excess of the Dilatation at a Point over the Mean Dilatation.*

Set off as abscissæ OA_1 OA_2 the areas s_1 and s_2 of the inner and outer boundaries of the section of the cylinder. As ordinates take the temperature θ of each narrow ring of internal area s, and draw the curve of temperature distribution throughout the section, fig. 5.

For each temperature estimate from tables of dilatation of the material, the dilatation a_θ of 1 c.c. of each part of the section, and with a_θ as ordinates, draw the curve of dilatation per cubic centimetre D to correspond to the temperature curve.
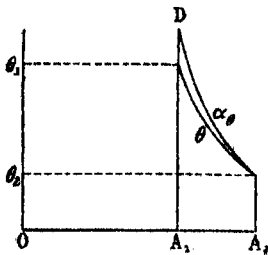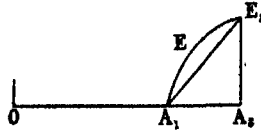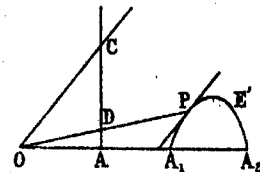
FIG. 5.   FIG. 6.   FIG. 7.

FIG. 5.—$OA_1 = s_1$, $OA_2 = s_2$, θ the curve of temperature, and a_θ that of dilatation.
FIG. 6.—The expansion curve E, $OA_1 = s_1$, $OA_2 = s_2$.
FIG. 7.—$A_1E'A_2$, the excess expansion curve ; OC parallel to the tangent at P ;
ADC a convenient ordinate.

Find the total expansion E of the shells within the radius r, if they had expanded independently of each other, that is, find the area enclosed between the axis of area, the curve D, the ordinate through A_1 and that through s for different values of s up to s_2, and plot the values obtained as ordinates against the areas as abscissæ. Join the end of the curve at E_2 with its starting point at A_1, fig. 6.

The excess of the ordinate of the curve at any point over the ordinate of the join is the ordinate of the excess expansion curve E′ required, fig. 7, the scale of ordinates being for convenience increased.

˙Join P a point on the curve to the origin O. Through O draw OB parallel to the tangent to the E′ curve at P and at A, corresponding to area s, a convenient multiple of 10, erect a perpendicular to the area axis cutting OB in C and OP in D_1.

Then the thermal stresses are given as follows :

$$R = \frac{1}{6}\frac{\epsilon}{1-\sigma} \cdot AD/OA, \qquad\qquad (3.1')$$

$$T = \frac{1}{6}\frac{\epsilon}{1-\sigma}(2AC - AD)/OA, \qquad\qquad (3.2')$$

$$X = \frac{1}{6}\frac{\epsilon}{1-\sigma}2\frac{AC}{OA}, \qquad\qquad (3.3')$$

$$\frac{r'}{r} = \frac{1}{6}\frac{1+\sigma}{1-\sigma}\frac{AD}{OA}, \qquad\qquad (3.4')$$

the mean pressure

$$\frac{1}{3}(R+T+X) = \frac{1}{6}\frac{\epsilon}{1-\sigma}\cdot\frac{4}{3}\cdot\frac{AC}{OA}, \qquad\qquad (3.5')$$

the shear stresses

$$\frac{1}{3}(X-T) = \frac{1}{6}\frac{\epsilon}{1-\sigma}\cdot\frac{1}{3}\frac{AD}{OA}, \qquad \frac{1}{3}(R-T) = \frac{1}{6}\frac{\epsilon}{1-\sigma}\cdot\frac{2}{3}\frac{AD-AC}{OA},$$

$$(3.6' \& 7')$$

and

$$\frac{1}{3}(R-X) = \frac{1}{6}\frac{\epsilon}{1-\sigma}\frac{1}{3}\cdot\frac{AD-2AC}{OA}. \qquad\qquad (3·8')$$

It will be noted that for the thermal stresses $R + T = X$ at any point, and since at the surfaces $R = 0$, $T = X$ at them both.

NUMERICAL EVALUATION OF STRESSES IN PRACTICAL CASES.

4. In applying the foregoing theory to practical problems it seems desirable to select in the first instance cases of a comparatively simple type in which the stresses due to mechanical causes are small. Two such cases are (1) that of a long pottery kiln, a section of which is kept at the firing temperature

either permanently or alternately with its neighbours, and (2) that of a circular pillar of concrete or of masonry supporting the ceiling of a warehouse in which a fire occurs.

Case (1) *a long Pottery Kiln or Furnace.*

5. The distribution of temperature throughout a cylinder concentrically heated and of length sufficient to make the effect of the ends negligible is determined by the equation

$$c\rho \frac{\partial \theta}{\partial t} = \frac{1}{r} \frac{\partial}{\partial r}\left(rk \frac{\partial \theta}{\partial r}\right). \tag{5.1}$$

If, in the first instance, we take the density ρ, the specific heat c and the heat conductivity k as constant, and the temperature distribution throughout the wall of the furnace as steady, θ_1 being the temperature of the inner surface at r_1, θ_2 that of the outer surface at r_2, we have

$$\frac{\theta - \theta_2}{\theta_1 - \theta_2} = \frac{\log r_2 - \log r}{\log r_2 - \log r_1} = \frac{\log s_2 - \log s}{\log s_2 - \log s_1}. \tag{5.2}$$

For simplicity we may take the dilatation α_θ proportional to the rise of temperature, that is $\alpha_\theta = \alpha\theta$. The expansion E of the rings between s_1 and s, if each expands independently of its neighbours, is given by $E = \int_{s_1}^{s} \alpha (\theta - \theta_2)\, ds$, and may be found either by graphic integration of the curve of temperature or directly from the equation

$$E = \alpha (\theta_1 - \theta_2)\frac{1}{\log s_2 - \log s_1}\{s(\log s_2 - \log s) - s_1(\log s_2 - \log s_1) + s - s_1\}, \tag{5.3}$$

and plotted as in fig. 8, where the temperature and the coefficient of $\alpha(\theta_1 - \theta_2)$ in E are shown for a cylinder when $s_1 = 0{\cdot}75s_2$. In that case the temperature curve is nearly linear.

The total expansion of the area of section of the kiln wall is given by the ordinate at A_2 of the E curve, fig. 8, and has the value

$$E_2 = \frac{\alpha (\theta_1 - \theta_2)}{\log s_2/s_1}\left\{ -s_1 \log \frac{s_2}{s_1} + s_2 - s_1\right\}.$$

The excess expansion $E' = E - E_2 \frac{s - s_1}{s_2 - s_1}$ is represented by the excess of the ordinate of the E curve over that of the join of the two ends of that curve in fig. 8 and is given by

$$E' = \alpha (\theta_1 - \theta_2)\left\{ s \frac{\log s_2 - \log s}{\log s_2 - \log s_1} - s_1 \frac{s_2 - s}{s_2 - s_1}\right\}. \tag{5.4}$$

The excess of the dilatation at any point over the mean dilatation for the whole wall is represented by the slope of the E' curve, and is given by

$$a\theta' = \frac{dE'}{ds} = a\,(\theta_1 - \theta_2)\left\{\frac{\log s_2 - \log s - 1}{\log s_2 - \log s_1} + \frac{s_1}{s_2 - s_1}\right\}.$$

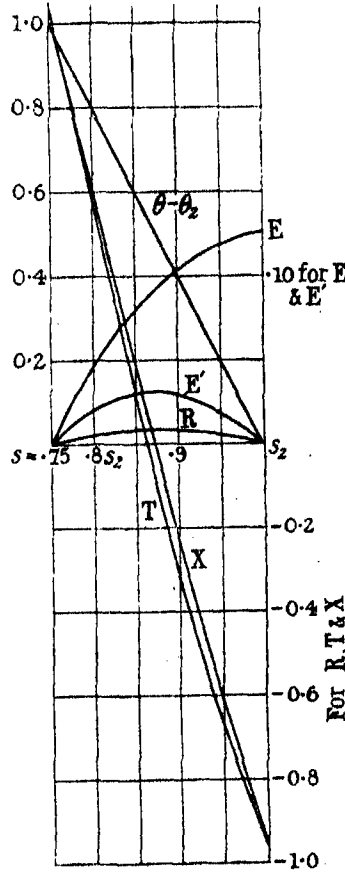On drawing the lines OP, OB and the vertical ADC, corresponding to fig. 7,

Fig. 8.—Temperature, expansion and stress curves for a hollow cylinder heated within.

or on substituting the values found above in the expressions for the thermal stresses and displacements, we get

$$R = \frac{1}{6}\frac{\epsilon}{1-\sigma}\cdot\frac{AD}{OA} = \frac{1}{6}\frac{\epsilon}{1-\sigma}a\,(\theta_1 - \theta_2)\left\{\frac{\log s_2 - \log s}{\log s_2 - \log s_1} - \frac{s_2/s - 1}{s_2/s_1 - 1}\right\}. \quad (5.5)$$

Thus the radial pressure is zero at the inner surface, rises to a maximum

$$\frac{1}{6}\frac{\epsilon}{1-\sigma}\cdot a\,(\theta_1 - \theta_2)\left\{\frac{1}{(s_2/s_1) - 1} + \frac{s_2}{s_1} - 1 - \frac{1}{\log s_2 - \log s_1}\right\}$$

at the section $s = s_1 s_2 \dfrac{\log s_2 - \log s_1}{s_2 - s_1}$, or $s = s_2 \dfrac{\log s_2/s_1}{(s_2/s_1) - 1}$, and becomes zero at the outer surface. If the outer temperature θ_2 is higher than the inner θ_1 these pressures become tensions.

In the same way the circumferential pressure T is given by

$$T = \frac{1}{6}\frac{\epsilon}{1-\sigma}\frac{2AC-AD}{OA} = \frac{1}{6}\frac{\epsilon}{1-\sigma}\alpha(\theta_1-\theta_2)\left\{\frac{s_2/s+1}{s_2/s_1-1} - \frac{2-(\log s_2 - \log s)}{\log s_2 - \log s_1}\right\}.$$

$$(5.6)$$

Thus the circumferential pressure is

$$\frac{1}{6}\frac{\epsilon}{1-\sigma}\alpha(\theta_1-\theta_2)\left\{\frac{2s_2}{s_2-s_1} - \frac{2}{\log s_2 - \log s_1}\right\}$$

at the inner surface r_1, becomes zero slightly within the ring of sectional area $(s_1 + s_2)/2$, and is $-\dfrac{1}{6}\dfrac{\epsilon}{1-\sigma}\alpha(\theta_1-\theta_2)\left\{-\dfrac{2s_1}{s_2-s_1} + \dfrac{2}{\log s_2 - \log s_1}\right\}$, that is a tension at the outer surface r_2.[*]

The longitudinal pressure X is given by

$$X = \frac{1}{6}\frac{\epsilon}{1-\sigma}\cdot 2\frac{AD}{OA} = \frac{1}{6}\frac{\epsilon}{1-\sigma}\alpha(\theta_1-\theta_2)2\left\{\frac{\log s_2/s - 1}{\log s_2/s_1} + \frac{s_1}{s_2-s_1}\right\}. \quad (5.7)$$

It changes from $\dfrac{1}{6}\dfrac{\epsilon}{1-\sigma}\alpha(\theta_1-\theta_2)2\left\{\dfrac{s_2}{s_2-s_1} - \dfrac{1}{\log s_2/s}\right\}$ at the inner surface

to zero at the surface $\dfrac{s}{s_2}\dfrac{1}{e}\left(\dfrac{s_2}{s_1}\right)^{s_1/(s_2-s_1)}$ and becomes

$$-\frac{1}{6}\frac{\epsilon}{1-\sigma}\alpha(\theta_1-\theta_2)2\left\{\frac{1}{\log s_2/s_1} - \frac{s_1}{s_2-s_1}\right\}$$

at the outer surface.

The thermal displacement other than that due to the mean rise of temperature is given by

$$\frac{r'}{r} = \frac{1}{2}\frac{s'}{s} = \frac{1}{6}\frac{1+\sigma}{1-\sigma}\frac{AD}{OA} = \frac{1}{6}\frac{1+\sigma}{1-\sigma}\cdot\alpha(\theta_1-\theta_2)\left\{\frac{\log s_2/s}{\log s_2/s_1} - \frac{s_2/s-1}{s_2/s_1-1}\right\}. \quad (5.8)$$

Thus the excess thermal displacement is zero at the two surfaces and has

its maximum value $\dfrac{1}{6}\dfrac{1+\sigma}{1-\sigma}\cdot\alpha(\theta_1-\theta_2)\dfrac{1}{\log s_2/s_1}\left\{\log\left(\dfrac{s_2/s_1-1}{\log s_2/s_1}\right)-1\right\}$ at the

surface $\dfrac{s}{s_2} = \dfrac{\log s_2/s_1}{s_2/s_1-1}$.

To this displacement must be added that due to the mean rise of

temperature which is given by $\dfrac{r'_0}{r} = \dfrac{1}{2}\dfrac{s'_0}{s} = \dfrac{1}{3}\alpha(\theta_1-\theta_2)\left\{\dfrac{s_2-s_1}{\log s_2/s_1} - s_1\right\}$.

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[*] The values of the tangential and axial stresses at the two surfaces are identical with those given by R. Lorenz, *loc. cit.*

The coefficients of $\frac{1}{6}\frac{\epsilon}{1-\sigma} . \alpha(\theta_1-\theta_2)$ in the expressions for the stresses are shown in fig. 8 as functions of s for the case $s_1 = 0.75s_2$. If $\theta_1-\theta_2 = 1000°$ C., the coefficient of cubical expansion of the material $\alpha = 12 \times 10^{-6}$, Young's modulus $\epsilon = 10^{11}$ and Poisson's ratio $\sigma = \frac{1}{3}$, the value of $\frac{1}{6}\frac{\epsilon}{1-\sigma}\alpha(\theta_1-\theta_2)$ is 3×10^8 dynes per sq. cm. The tensile strength of fire brick is of the order 2×10^7 dynes per square centimetre (300 lbs. per square inch). The tensions T and X in the outer portion of the wall are, therefore, capable of producing cracks in the material which will be radial, and, since at the outer surface T and X are equal, will extend in the longitudinal as often as in the transverse direction.

6. If the temperature throughout the section is not steady but variable, the number of possible distributions is infinite, but of these cases two are worth investigating as of practical value (A) when the kiln or furnace initially at θ_2 has its inner surface raised at a given instant to θ_1, and (B) when a kiln or furnace has been in operation with its inner surface at θ_1 and its outer at θ_2 for a considerable time, and at a given time has the temperature of its inner surface reduced to θ_2.

A. The kiln is brought into service.

For the first few minutes the only change of temperature is that close to the inner surface. The mean temperature is scarcely changed from θ_2, the E' curve has very small ordinates but θ' has approximately the value $\theta_1 - \theta_2$ close to the inner surface.

Hence at this stage, close to the inner surface, R the radial pressure and r'/r the radial displacement are very small, but T the tangential and X the longitudinal pressures are both very nearly double what they finally become in the steady state, that is near the inner surface they both have initially the value

$$\frac{1}{3}\frac{\epsilon\alpha}{1-\sigma}(\theta_1-\theta_2),$$

and decrease to half that value as the temperature distribution approaches that of the steady state.

B. The kiln is put out of service.

For the first few minutes the only change of temperature will be at the inner surface. The mean temperature of the section is scarcely changed and the E' curve has only a very small negative ordinate near its zero value at the inner surface. The approximate value of θ' at the inner surface is changed from $(\theta_1-\theta_2)/2$ to $-(\theta_1-\theta_2)/2$.

Thus R the radial pressure and r'/r the radial displacement are very small close to the inner surface; but T the tangential pressure and X the longitudinal pressure change from the approximate value $\frac{1}{6}\frac{\epsilon\alpha}{1-\sigma}(\theta_1-\theta_2)$ to

$-\frac{1}{6}\frac{\epsilon\alpha}{1-\sigma}(\theta_1-\theta_2)$, that is from pressures to equal tensions.

We have seen that, for a furnace with a difference of temperature of 1000° C. between inside and outside surfaces of the walls, composed of material with a coefficient of cubical expansion $\alpha = 12 \times 10^{-6}$, a Young's modulus ϵ of 10^{11} and a Poisson's ratio σ of $\frac{1}{4}$, the value of $\frac{1}{12}\frac{\epsilon\alpha}{1-\sigma}(\theta_1-\theta_2)$ is $1\cdot5 \times 10^8$ dynes per square centimetre (2250 lb. per square inch), while the tensile strength of the material of the walls is of the order of 2×10^7 dynes per square centimetre (300 lb. per square inch), and that of the mortar about one-fifth of this. The sudden cooling of the interior of a furnace such as that described above will therefore subject the interior of the wall to tensile stresses in both longitudinal and tangential directions much above the tensile strength of the material, and radial cracks will be produced at the inner surface, which, since the stresses are equal in the two directions, will run indiscriminately longitudinally and tangentially.

Through the kindness of Sir Robert Hadfield, I have been able to inspect the walls of furnaces which have been in use for various periods at the Hecla Works, Sheffield, and I find that the above results are confirmed by experience.

Case 2.—A Concrete or Masonry Pillar subjected to Fire.

7. A circular pillar of radius a, initially at a uniform temperature 0°, has its outer surface suddenly raised to θ_a.

Assuming that the physical constants of the material of the pillar may be taken as uniform throughout the material, the distribution of temperature throughout the centre length of the pillar at any subsequent time will be given by the equation

$$\frac{\partial\theta}{\partial t} = \frac{k}{c\rho}\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial\theta}{\partial r}\right). \tag{7.1}$$

The solution of which under the conditions laid down is

$$\theta = \theta_a - 2\theta_a \sum_\beta e^{-k/c\rho\,(\beta_n/a)^2 t} \cdot \frac{J_0(\beta_n r/a)}{\beta_n J_1(\beta_n)}* \tag{7.2}$$

where $J_0(\beta)$ is the Bessel function of zero order, $J_1(\beta)$ that of the first order, and the β's are the roots of the equation $J_0(\beta) = 0$.

* Compare Byerley, ' Fourier Series and Spherical Harmonics,' p. 229.

For a disc of the pillar initially 1 cm. thick cut perpendicular to the axis we therefore have

$$E = \int_0^r 2\pi r\, dr\, \alpha\theta = 2\pi\alpha\theta_a \left\{ \frac{r^2}{2} - 2\Sigma e^{-k/c\rho\, (\beta_n/a)^2 t} \cdot \frac{ar \cdot J_1(\beta_n r/a)}{\beta_n{}^3 J_1(\beta_n)} \right\}.$$

Hence at $r = a$

$$E_a = 2\pi\alpha\theta_a \left\{ \frac{a^2}{2} - 2\Sigma e^{-k/c\rho\, (\beta_n/a)^2 t} \cdot \left(\frac{a}{\beta_n} \right)^2 \right\}$$

and

$$E' = E - E_a \cdot \frac{r^2}{a^2} = 4\pi\alpha\theta_a \Sigma e^{-k/c\rho\, (\beta_n/a)^2 t} \cdot \frac{r^2}{\beta_n{}^3} \left\{ 1 - \frac{J_1(\beta_n r/a)}{\beta_n r/a} \cdot \frac{\beta_n}{J_1(\beta_n)} \right\}.$$

$$(7.3)$$

Hence the stresses are given by the equations

$$R = \frac{1}{6} \frac{\epsilon}{1-\sigma} \cdot \frac{E'}{\pi r^2} = \frac{2}{3} \cdot \frac{\epsilon}{1-\sigma} \cdot \alpha\theta_a \Sigma e^{-k/c\rho\, (\beta_n/a)^2 t}$$

$$\cdot \frac{1}{\beta_n{}^2} \left\{ 1 - \frac{J_1(\beta_n r/a)}{\beta_n r/a} \cdot \frac{\beta_n}{J_1(\beta_n)} \right\}, \quad (7.4)$$

$$T = \frac{1}{6} \frac{\epsilon}{1-\sigma} \left(2 \frac{dE'}{2\pi r\, dr} - \frac{E'}{\pi r^2} \right) = \frac{2}{3} \frac{\epsilon}{1-\sigma} \alpha\theta_a \Sigma e^{-k/c\rho\, (\beta_n/a)^2 t}$$

$$\cdot \left\{ \frac{1}{\beta_n{}^2} - \frac{1}{J_1(\beta_n)} \left[\frac{1}{\beta_n} J_0\left(\frac{\beta_n}{a} r \right) - \frac{a}{r} J_1\left(\frac{\beta_n}{a} r \right) \right] \right\}, \quad (7.5)$$

$$X = \frac{1}{6} \frac{\epsilon}{1-\sigma} 2 \frac{dE'}{2\pi r\, dr} = \frac{2}{3} \frac{\epsilon}{1-\sigma} \alpha\theta_a \Sigma e^{-k/c\rho\, (\beta_n/a)^2 t}$$

$$\left\{ \frac{2}{\beta_n{}^2} - \frac{1}{\beta_n J_1(\beta_n)} \cdot J_0\left(\frac{\beta_n}{a} r \right) \right\}, \quad (7.6)$$

and the expansion by the equation

$$\frac{r'}{r} = \frac{1}{2} \frac{s'}{s} = \frac{2}{3} \frac{1+\sigma}{1-\sigma} \cdot \alpha\theta_a \Sigma e^{-k/c\rho\, (\beta_n/a)\, t} \frac{1}{\beta_n{}^2}$$

$$\left\{ 1 - \frac{J_1(\beta_n r/a)}{\beta_n r/a} \cdot \frac{\beta_n}{J_1(\beta_n)} \right\} + \frac{1}{3} \alpha\theta_a \left\{ 1 - 4\Sigma \frac{1}{\beta_n{}^2} e^{-k/c\rho\, (\beta_n/a)^2 t} \right\}, \quad (7.7)$$

the last term representing the expansion due to the mean rise of temperature.

It will be noticed that $T + R = X$, that is, the stress in the axial direction at a point is equal to the sum of the radial and tangential stresses at the point.

8. These expressions are convenient solutions of the problem when t, the time which has elapsed since the outer surface of the pillar was first heated, is sufficiently large to reduce each series to its first term, but, in general, the series converge very slowly, and many terms must be taken before an accurate numerical result is obtained.

As it is in the earlier stages of the heating, before the temperature near the middle of the pillar has commenced to rise, that the thermal stresses appear to produce their greatest effect, it is desirable to attempt to represent

the temperature distribution for small values of t by a simpler expression, which will reproduce the principal characteristics of the actual case.

We have found

$$E' = 4\pi a \theta_a \Sigma e^{-k/c\rho (\beta_n/a)^2 t} \cdot \frac{r^2}{\beta_n^2} \left\{ 1 - \frac{J_1(\beta_n r/a)}{\beta_n r/a} \cdot \frac{\beta_n}{J_1(\beta_n)} \right\}.$$

Now $$J_1\left(\frac{\beta_n}{a} r\right) = \frac{\beta_n}{2a} r \left\{ 1 - \frac{1}{2}\left(\frac{\beta_n r}{2a}\right)^2 + \frac{1}{12}\left(\frac{\beta_n r}{2a}\right)^4 - \dots \right\}.$$

Substituting we find

$$E' = 4\pi a \theta_a \Sigma e^{-k/c\rho (\beta_n/a)^2 t}$$

$$\cdot \frac{r^2}{\beta_n^2} \frac{-\frac{1}{2}(\beta_n/2)^2 (a^2 - r^2)/a^2 + \frac{1}{12}(\beta_n/2)^4 (a^4 - r^4)/a^4 - \dots}{1 - \frac{1}{2}(\beta_n/2)^2 + \frac{1}{12}(\beta_n/2)^4}, \quad (8.1)$$

and on substituting s/s_a for r^2/a^2

$$E' = -a\theta_a s \cdot \Sigma e^{-k/c\rho \cdot (\beta_n/a)^2 t} \cdot \frac{\frac{1}{2}(s_a - s)/s_a - \frac{1}{12}(\beta_n/2)^2 (s_a^2 - s^2)/s_a^2 - \dots}{1 - \frac{1}{2}(\beta_n/2)^2 + \frac{1}{12}(\beta_n/2)^4 - \dots}.$$

The form of this expression suggests the assumption that at any time during the early stages of the heating process the value of E may be taken as approximating to $\frac{a\theta_a}{n+1} \cdot s \left(\frac{s}{s_a}\right)^n$ where n has a value which decreases as t increases. Then

$$E' = -\frac{a\theta_a}{n+1} s \cdot \left[1 - \left(\frac{s}{s_a}\right)^n \right], \quad (8.2)$$

$$\theta' = \frac{\theta_a}{n+1} \left\{ 1 - (n+1)\left(\frac{s}{s_a}\right)^n \right\}, \qquad \bar{\theta} = \frac{\theta_a}{n+1},$$

and the values of the stresses and displacements are readily seen to be

$$R = -\frac{1}{6} \frac{\epsilon}{1-\sigma} \cdot \frac{a\theta_a}{n+1} \left\{ 1 - \left(\frac{s}{s_a}\right)^n \right\}, \quad (8.3)$$

$$T = -\frac{1}{6} \frac{\epsilon}{1-\sigma} \cdot \frac{a\theta_a}{n+1} \left\{ 1 - (2n+1)\left(\frac{s}{s_a}\right)^n \right\}, \quad (8.4)$$

$$X = -\frac{1}{6} \frac{\epsilon}{1-\sigma} \cdot \frac{a\theta_a}{n+1} \left\{ 2 - 2(n+1)\left(\frac{s}{s_a}\right)^n \right\}, \quad (8.5)$$

$$\frac{r'}{r} = \frac{1}{2}\frac{s'}{s} = -\frac{1}{6}\frac{1+\sigma}{1-\sigma}\frac{a\theta_a}{n+1} \left\{ 1 - (n+1)\left(\frac{s}{s_a}\right)^n \right\} + \frac{1}{3}\frac{a\theta_a}{n+1}, \quad (8.6)$$

the last term giving r'/r for the mean rise of temperature $\bar{\theta}$.

Thus the mean temperature $\bar{\theta}$ increases as n decreases.

The radial stress R is zero at the surface, is a tension within, which increases in value rapidly towards its maximum value $-\frac{1}{6}\frac{\epsilon}{1-\sigma} \cdot \frac{a\theta_a}{n+1}$ at the

centre and has nearly that value for a considerable distance from the centre if n is large.

The tangential stress T has the value $\dfrac{1}{6}\dfrac{\epsilon}{1-\sigma}\cdot\dfrac{\alpha\theta_a}{n+1}\ 2n$ and is a pressure at the surface, decreases to zero at the section $\left(\dfrac{s}{s_a}\right)^n=\dfrac{1}{2n+1}$ becomes a tension and has the value $-\dfrac{1}{6}\dfrac{\epsilon}{1-\sigma}\cdot\dfrac{\alpha\theta_a}{n+1}$ at the centre, attaining nearly that value at a considerable distance from the centre if n is large.

The axial stress X has the value $\dfrac{1}{6}\dfrac{\epsilon}{1-\sigma}\cdot\dfrac{\alpha\theta_a}{n+1}\cdot 2n$ and is a pressure at the surface, decreases to zero at the section $\left(\dfrac{s}{s_a}\right)^n=\dfrac{1}{n+1}$ becomes a tension and has the value $-\dfrac{1}{6}\dfrac{\epsilon}{1-\sigma}\cdot\dfrac{\alpha\theta_a}{n+1}\cdot 2$ at the centre, attaining nearly that value at a considerable distance from the centre if n is large.

The displacement term r'/r has the value $\dfrac{\alpha\theta_a}{n+1}\left(\dfrac{1}{3}+\dfrac{n}{6}\dfrac{1+\sigma}{1-\sigma}\right)$ at the surface and the displacement r' decreases to zero at the centre.

The curves of fig. 9 give the coefficients of $\dfrac{1}{6}\dfrac{\epsilon}{1-\sigma}\cdot\dfrac{\alpha\theta_a}{n+1}$ in the expressions for the stresses for the case $n=8$. The curve for the axial stress X shows also the distribution of temperature above and below the mean temperature, and with the coefficient $\dfrac{1}{3}\dfrac{1+\sigma}{1-\sigma}\cdot\dfrac{\alpha\theta_a}{n+1}$ that part of the expression for the displacement term r'/r which depends on the variation of the temperature from the mean temperature.

During the early stages of the heating, the longitudinal tension X in the central portion of the section is double the radial tension R and the tangential tension T. If the pillar is not subject to other mechanical stresses, and the magnitude of these thermal stresses approaches the tensile strength of the material, cracks in planes perpendicular to the axis of the cylinder will be more frequent in the central portions than cracks in other directions.

As, however, the tensile strength of most materials is less at high than at low temperatures, it is possible that the radial tension, which persists, but with diminished magnitude in the outer and hotter layers near the surface, where the tangential and longitudinal stresses have become pressures, may still be large enough in these layers to exceed the tensile strength of the material. In any layers in which this is the case, cracks will be formed parallel to the outer surface of the cylinder.

The tangential tension T, like the radial tension R, is half the longitudinal tension X in the central portions of the section, but becomes zero, and then a
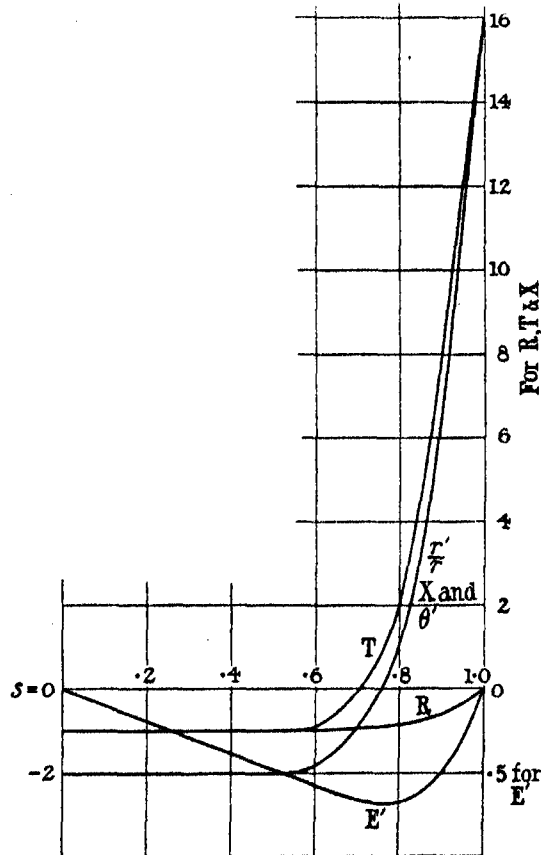

FIG. 9.—Temperature, expansion and stress curves for circular pillar, heated outside, in case $n = 8$.

pressure in the outer portions, where R is still a tension. Hence the tendency for cracks parallel to the axis to form during the heating process is less than for cracks perpendicular to the axis in the central portions, and less than for cracks parallel to the outer surface in the outer portions.

A Heated Solid Cylinder has its Surface Suddenly Cooled.

9. In this case the stresses and displacements are identical in magnitudes with those determined for the heating of the cylinder, but the sign of each is changed, a pressure becoming a tension and a tension a pressure. In fig. 9 we may consider the signs of the ordinates reversed. At the stage of the cooling shown, which we may regard as representative for the earlier stages,

the greatest tensile stress is the tangential one, T, which, except just at the surface, is slightly larger than the axial tensile stress X, and decreases rapidly in magnitude as we approach the centre.   While T and X are both tensions, the radial pressure R is positive—that is a pressure.   During cooling, we see, then, that there will be a slightly greater tendency for T to form cracks running parallel to the axis than for X to form cracks running round the cylinder.

There will be no tendency for R to form cracks running parallel to the outer surface of the cylinder.

In comparing the stresses produced on cooling with those due to heating, it must not be assumed in general that the contraction on cooling is identical with the dilatation on heating.   As a rule, building materials expand more on first being heated than they do at any subsequent heating, and after each heating contract on cooling by a less amount than they expanded.   Each heating and cooling results in a permanent increase of volume, which decreases in magnitude with each successive change.*   In such cases it is therefore necessary to use the general theory of Section 2.

10. It is difficult to find experimental observations with which to compare the above deductions.   The only tests of cylinders subjected to fire without mechanical loading appear to be those of W. A. Hull of the Bureau of Standards,† which were carried out on cylinders of clay, concretes, gypsums and mortars 8 inches in diameter and 16 inches long, heated in a gas furnace for 3½ hours to 927° C. (1700° F.).   These cylinders are too short to justify the neglect of the effect of the end surfaces, but the temperatures are of the order of those used in the numerical work of this paper.   Mr. Hull draws no general conclusions as to the tendency of the cracks, but the illustrations show a tendency for the major cracks to run in planes perpendicular to the axis.

For longer vertical cylinders under mechanical stress due to a load carried by the cylinder, the observations of Hull‡ appear to be the only ones available for comparison.   These columns were 12 or 18 inches in diameter 8 feet 9 inches long, of various materials, and were heated for 4 hours in a gas furnace to 1100° C. while under load.   Both plain and reinforced concrete columns were tested.

In this case in addition to the longitudinal thermal stress X there was the

* See Day, Sosman and Hostetter, 'Amer. Jour. Sci.,' vol. 37, p. 1 (1914) ; and Mellor and Campbell, 'Trans. Ceramic Soc.,' vol. 15, p. 80 (1915), and references given by them.

† W. A. Hull, "Heat Insulating Properties of Materials," 'Proceedings of the American Society for Testing Materials,' Philadelphia, June, 1917.

‡ See W. A. Hull, "Fire Tests of Concrete Columns," 'Proceedings of the American Concrete Institute,' vol. 15, p. 1 (1918).

stress due to the load which, in the case of the plain concrete columns, was of the order of 800 lbs. per square inch.

According to the curves of temperature distribution given by Hull, the curves of fig. 9 correspond approximately to the state half an hour after the heating commenced. With the constants for concrete taken as $\alpha = 4 \times 10^{-5}$, $\epsilon = 1 \times 10^{11}$, $\sigma = 1/3$, the value of the coefficient $\frac{1}{6} \frac{\epsilon}{1-\sigma} \cdot \frac{\alpha \theta_a}{n+1}$ of the equations (8.4, etc.) and of the ordinates of the curves of fig. 9 is $1\cdot2 \times 10^8$ dynes per square centimetre (1800 lbs. per square inch). Thus in the central portion of the section of the column the thermal stresses R and T are tensions of $1\cdot2 \times 10^8$ dynes per square centimetre and X a tension of double that amount. The latter has to be diminished by the pressure due to the load and we get a resultant tension of about 2800 lbs. per square inch, which is greater than the radial and tangential tensions. There will, therefore, be a greater tendency for cracks to form perpendicular to the axis in the central parts of a column than in other directions. In the outer portion of the section the tangential stress T becomes a pressure before the radial R, and neither are affected by the loading. In these portions R is more likely to form cracks parallel to the outer surface than T is to form cracks parallel to the axis. The positions of the cracks due to R will be determined by the decrease of the tensile strength of the concrete as the temperature rises. The curves of fig. 9 show that from $s/s_a = 0\cdot6$ to $0\cdot8$ while R decreases little the temperature increases considerably and the tensile strength therefore decreases.

Hull's observations and photographs all indicate that the materials crack along a surface about $1\frac{1}{2}$ to 2 inches within the outer surface (s/s_a, $0\cdot6$), and that the outer shell may, or may not, fall away. The existence of these cracks within columns which have been subjected to fire, but which appear on the surface uninjured, has been known for some time.[*]

As the tensile strength of concrete, at ordinary temperatures, is of the order 1×10^8 dynes per square centimetre (1,500 lbs. per square inch), it is seen that the thermal stresses in the heated columns, at the stage of the heating represented by fig. 9, are sufficient to account for the cracks produced.

As the heating continues the tensions in the central portion of the section at first increase, while the area subjected to them decreases. When the temperature at the centre begins to rise the stresses decrease.

Where the column is reinforced with vertical rods, with or without

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[*] See F. J. T. Stewart, 'Report on Edison Works Fire,' Scientific and Industrial Research Department, British Fire Prevention Committee's Red Book No. 204, p. 28 (1916); and A. J. and T. D. Mylrea, 'Report on Quaker Oats Works Fire,' British Fire Prevention Committee's Red Book No. 225, p. 56 (1918).

horizontal binders, the crack produced follows the rods or binders, indicating that the tensile strength of attachment of metal to concrete is less than that of the concrete itself at the temperature attained.

So soon as the outer shell is detached from the inner portion it has to carry its share of the load without lateral support from the inside. It therefore buckles like an overloaded hollow column and eventually spalls off.

During the cooling process which, in Hull's experiments, was a gradual one, and began long before the column had wholly acquired the higher temperature, vertical cracks, starting at the outside surface and extending inwards, would be most likely to form. The tendency would be the greater the more rapid the cooling, but less than it would be if the whole column had acquired the higher temperature before cooling. The photographs of the columns, after the tests given by Hull, nearly all show these vertical cracks,* but there is no indication as to whether they were produced during the cooling or not.

So far as the experimental evidence available goes it appears to support the theoretical deductions of this paper, but it is desirable that the thermal stresses should be computed either graphically or otherwise in all cases in which the necessary observations are available, in order to determine to what extent the explanation of the behaviour of furnace walls and columns here offered is adequate.

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* W. A. Hull, 'Tests of Concrete Columns,' p. 15. An important contribution to our knowledge of the effects of fire and water on loaded columns has just been made by Messrs. Ingberg, Griffin, Robinson and Wilson. See ' Bureau of Standards Technological Paper No. 184 ' (1921).

On Errors arising in the Measurement of Unsymmetrical Spectrum Lines.

By T. R. MERTON, D.Sc., F.R.S., Professor of Spectroscopy in the University of Oxford, and D. N. HARRISON, Scholar of Balliol College, Oxford.

It is generally recognised that one of the most serious sources of error in relative determinations of the wave-lengths of spectrum lines by micrometric measurements of the positions of the lines on photographic plates lies in the mechanical and other displacements, which result in errors in the super-position or juxtaposition of the spectrum under investigation and the standard spectrum, the wave-lengths of which are supposed to be known. Thus, if a spectrum to be measured is photographed on a plate and an iron arc spectrum is then photographed in juxtaposition, an error may arise, either from some flexure or mechanical displacement between the two exposures or from a gradual change of temperature of the dispersing prism or grating, resulting in a continuous drift of the spectrum across the plate. Even when the utmost care is taken to avoid these displacements by rigid design of the spectrograph and proper control of temperature, it is hardly ever possible to eliminate them entirely, and it is necessary to follow some procedure which will reduce the errors arising from them to a minimum.

A method which is commonly used is to expose the comparison spectrum in two parts. For example, a comparison spectrum with one-half the total exposure required may be taken first; the spectrum to be measured is then exposed for an appropriate time, and finally the second half-exposure of the comparison spectrum is superposed on the first. Images of the comparison lines (and in the case of a long exposure of the lines to be measured) would be somewhat broadened, but it might at first seem that the maxima of the lines in the two spectra would be in correct juxtaposition, supposing that there has been a constant drift of the spectrum across the plate owing to a gradual change of temperature. St. John and Babcock,[*] in a study of the pole effect in the iron arc, used a system of reflecting prisms to project on the slit simultaneously the light from the neighbourhood of the pole in juxta-position with that from the centre of the arc, the intensities being equalised by means of a rotating sector, which occulted for an appropriate period the more intense light from the neighbourhood of the pole.

It might at first appear that in the case in which a source emitted both

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[*] 'Astrophys. Journ.,' vol. 42, p. 231 (1915).

standard lines and the lines under investigation the errors due to displacements would be entirely innocuous.   It is unfortunate that this is true only for the special case in which the lines of both spectra are symmetrical, and it is by no means certain that this condition is ever fulfilled, excepting in the case of the spectra of gases contained in vacuum tubes at low pressures and excited by uncondensed discharges, where the sole cause of broadening is known to be that due to the motions of the radiating particles in the line of sight operating in accordance with Doppler's principle.   Although it is obvious that errors must arise in the case in which the lines are not symmetrical, their importance does not appear to have been recognised fully.

As an illustration of the extreme case we may consider (fig. 1) two symmetrical lines with maxima at a, a, and between them a completely unsymmetrical line with maximum at b, the ordinates representing the intensity
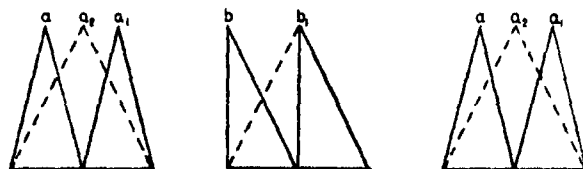
Fig. 1.

and the abscissæ the wave-length scale.   If during an exposure the lines drift across the photographic plate with uniform velocity, so that at the end of the exposure their true maxima lie at a_1, a_1, and b_1, it is clear that on the photographic plate the maxima will appear to be at a_2, a_2, and b_1, and if a, a, are used as standards for determining the wave-length of b, the wave-length so found will be in error by as much as one-half of the total shift.   It is assumed that in the measurement of spectrograms the cross-wires of the microscope are set on the blackest part of the line, but a discussion of the extent to which this is reached in practice is beyond the scope of the present note.

The above example is given merely to illustrate the principles on which the errors arise, and although the displacements which occur in practice must be of so varied a character that it is not possible to discuss them in detail, it is of interest to consider the case of a uniform displacement, and it will be shown that the errors can be expressed in a general form which is independent of the intensity distribution.   In a previous investigation* the limitation which the resolving power of the spectroscope imposes on the accuracy of wave-length determinations of unsymmetrical lines has been considered, and it was found convenient to represent the intensity distribution of lines by the

* Nicholson and Merton, 'Roy. Soc. Proc.,' A, vol. 98, p. 261 (1920).

law $I = e^{-kx^2}$, the asymmetry being reproduced by adopting different values of k on the two sides of the maximum. It is convenient to define as the "index of symmetry," I, the ratio of the "half-widths" x_1, x_2, on either side of the maximum, these being the values of x which make I equal to $\frac{1}{2}$, the value of I at the maximum being taken as unity.

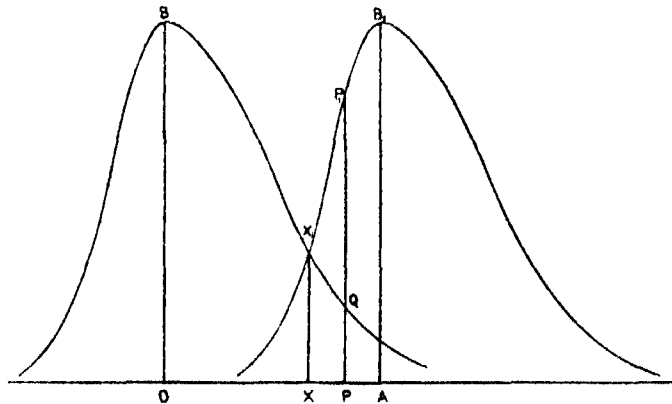In fig. 2 the unsymmetrical line having a maximum at O is supposed to move with uniform velocity during an exposure, until at the end of the

Fig. 2.

exposure the maximum lies at A. The position of the maximum on the plate lies at the intersection of the two intensity-distribution curves at the beginning and end of the exposure. It can easily be shown that this result is perfectly general if the curves intersect, and is independent of their shape. The intensity at X is proportional to the area bounded by OBX_1B_1A and is smaller at any other point. Thus at P the intensity is proportional to the areas $OBQP + PP_1B_1A$, and is evidently less than the intensity at X by an amount proportional to the area X_1P_1Q. In the particular case in which the two values of X for each intensity are in a constant ratio, *e.g.*, if the curve is of the exponential form given above, the position of the maximum is given by $OX/XA = x_1/x_2$, and $OX = OA/(1 + x_2/x_1) = OA/(1 + 1/I)$.

From this result it follows, for example, that if the index of asymmetry of such a line were equal to 5, an error of one-third of the displacement would result in the determination of its wave-length by comparison with two symmetrical lines on either side of it.

One of the main causes of the broadening of spectrum lines is that due to the electrical resolution of the lines, caused by the electric field of neighbouring charged particles on the radiating atoms, and since in a number of cases the effect of the electric field is to produce a simple displacement to one side, or

a resolution into components on one side only, the index of asymmetry for such lines might be very great. In the case of a broadening due to this cause, the constancy of the ratio of the two values of x for any intensity follows from the proportionality which is usually found between the intensity of the electric field and the resolution of the lines.

St. John and Babcock (*loc. cit.*) in their investigation of the pole effect have made use of the ingenious device of inserting a bulb containing iodine at a low pressure between the iron arc and the spectrograph, and a number of lines were found to have one or more very narrow iodine absorption lines superposed on them. This procedure, however, does not automatically eliminate the errors arising from instrumental displacements, and it can be shown that if the emission line is unsymmetrical and a displacement occurs during the course of the exposure, the minimum of the absorption line, actually lying on one side of the emission maximum, may appear on the plate on the other side of the maximum.

It seems that instrumental displacements can be rendered innocuous only in the case of spectra whose lines are known to be symmetrical, such as the spectra of gases at low pressures referred to above, and such spectra are, therefore, to be preferred as standards of wave-lengths, rather than arc spectra at atmospheric pressure, where it is known that many of the lines are unsymmetrical. The asymmetry of the lines in arc spectra may depend on the density of the vapour in the arc, but in measurements of such lines displacements will have the effect that all the errors will be in the direction in which the lines show asymmetry. This may indeed be contributory to the fact that there are series of lines which cannot be represented satisfactorily by any of the formulæ which are generally used to connect the individual members of spectrum series, for Royds[*] has shown that in some series the earlier members may show asymmetry in one direction whilst in the later members the direction of the asymmetry is reversed.

These considerations seem to be relevant in all cases where the detection and measurement of minute changes of wave-length are involved. It is to be regretted that at the present time we have very little precise information as to the distribution of intensity in broadened spectrum lines, but it is possible that micrometric measurements may be carried sometimes to a higher degree of precision that the rigidity and efficiency of temperature control of the spectrograph can justify.

[*] 'Astrophys. Journ.,' vol. 41, p. 154 (1915).

On the Use of Very Small Pitot-Tubes for Measuring Wind Velocity.

By Muriel Barker, B.Sc., Newnham College, Cambridge.

Introduction.

A recent paper by Stanton and Marshall[*] describes experiments made to determine the distribution of velocity close to the wall of a pipe through which air in a turbulent state is flowing. In order to measure the velocity of the air, Stanton used a very fine Pitot-tube placed in the pipe so that it faced the wind.

There is plenty of evidence that Pitot-tubes used in ordinary aeronautical work do provide an accurate measure of wind speed, the excess of pressure inside the tube over that in the surrounding air being $\frac{1}{2}\rho v^2$, where ρ is the density and v the velocity of the air. On the other hand, there are two factors which would lead one to expect that this law might not hold under the conditions which occurred in Stanton's experiment.

In the first place, the wind velocity is varying very rapidly across the mouth of the Pitot-tube. If, therefore, the formula $p = \frac{1}{2}\rho v^2$ be applied to determine v from the measured value of p, the exact position of the layer of fluid which would be flowing with velocity v, if it were undisturbed by the Pitot-tube, is a matter of doubt.

In Stanton's experiment this difficulty is accentuated, because, in order to obtain measurements very close to the wall, he uses a Pitot-tube which has only one side, the other being replaced by the wall itself. In such a tube, the "v" to be used in the formula $p = \frac{1}{2}\rho v^2$ might be expected to lie between zero and the velocity at the level of the outer wall of the Pitot-tube. This may be expressed by saying that the "effective distance" of the Pitot-tube from the wall is less than the total opening of the one side of the Pitot-tube. The "effective distance" is defined as the distance from the wall at which the air moves with velocity $\sqrt{(2p/\rho)}$, p being the pressure in the Pitot-tube.

In the second place, when a very small tube is used, or when wind speed is very low, one might expect that p would be proportional to v rather than to v^2.

Stanton in his experiment gets over both these difficulties at once by first using his Pitot-tube in a pipe through which air is flowing in stream-line

motion. Under these conditions the distribution of velocity in the pipe is known. The Pitot-tube can therefore be calibrated. The calibration consists in determining the " effective distance " of the Pitot-tube from the wall for various openings.

Stanton found that the " effective distance " of his Pitot-tube from the wall was connected with the total opening by a linear relation. It was found, however, that the straight line which represents the results does not pass through the origin, so that there appears to be a finite " effective distance " corresponding with the zero velocity which is known to occur at the wall. This result might have been anticipated.

It is possible to carry the matter further however. Suppose we assume that the pressure at the centre of Stanton's one-sided Pitot-tube is the same as that at the nose of a sphere, of the same diameter as the opening of the Pitot-tube, when placed in a stream moving with a velocity equal to that at the centre of the Pitot opening. The velocity at the centre of the Pitot opening, assuming stream-line flow, is $\bar{v}$, where

$$\bar{v} = v_0 \left\{ 1 - \frac{(a-d)^2}{a^2} \right\} = v_0 \frac{(2a-d)\,d}{a^2}, \tag{1}$$

where v_0 is the velocity at the centre of the pipe, a its radius, and $2d$ the breadth of the Pitot opening.

On the assumption made above, the pressure p in the Pitot-tube would be, by Stokes' law,

$$p = \frac{3}{2} \frac{\mu \bar{v}}{d} = \frac{3}{2} \mu v_0 \left\{ \frac{2}{a} - \frac{d}{a^2} \right\} \tag{2}$$

from (1), μ being the coefficient of viscosity.

On this assumption, therefore, it will be seen that the pressure tends to a constant value $3\mu v_0/a$ when d tends to zero. The " effective distance," which will be denoted by d', corresponding with this pressure, is the distance from the wall at which the velocity is equal to $\sqrt{(2p/\rho)}$. Since the rate of shear close to the wall is $2v_0/a$, we have

$$\frac{2v_0}{a} d' = \sqrt{\left(\frac{2p}{\rho}\right)} = \sqrt{\left(\frac{6\mu v_0}{a\rho}\right)}$$

whence
$$d' = \sqrt{\left(\frac{3\mu a}{2\rho v_0}\right)}. \tag{3}$$

In Stanton's case the experiments were made with a pipe at three different velocities of v_0, *i.e.*, 1910, 1140, and 740 cm. per second. Using the values $\mu/\rho = 0.148$, $a = 0.1345$ cm., equation (3) gives the following values for d', namely, 0.0039, 0.0051, and 0.0063 cm.

The results of Stanton's calibration experiments are shown in fig. 1. In

this diagram the abscissæ represent the opening of the one-sided Pitot-tube while the ordinates represent the "effective distance." It will be seen that, when the opening tends to zero, the "effective distance" tends to 0·005 cm. approximately. This value lies within the range of the values calculated above.

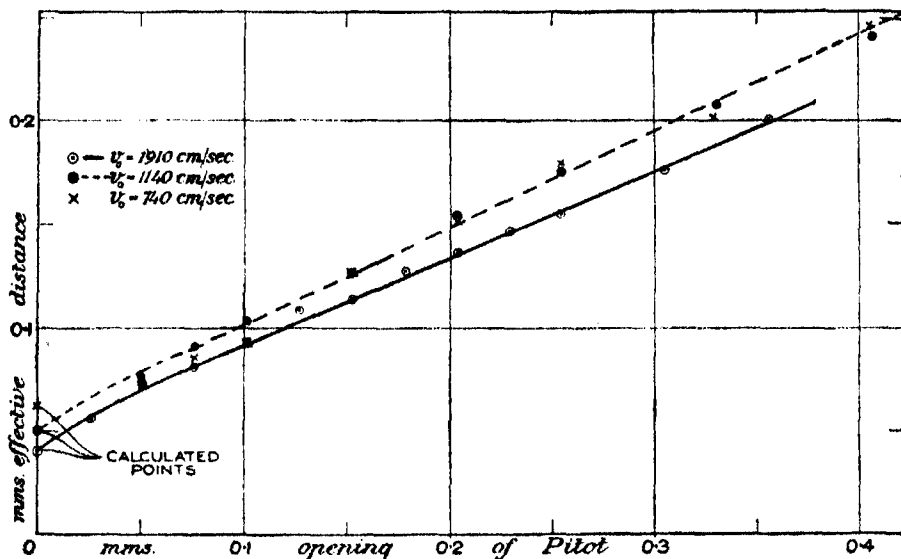Stanton obtains one mean calibration curve from his three sets of results

Fig. 1.

Diameter of pipe, 0·269 cm.   Pitot-tube No. 3.

at different velocities.   Formula (3), however, indicates that d' is not independent of v_0.   This might be expected from a consideration of the theory of dimensions.   In fact, the points obtained by Stanton, when $v_0 = 1910$ and 1140 cm. per second respectively, do lie on different lines as shown in fig. 1, and the points where these lines cut the y axis correspond very fairly to the ones calculated from Formula (3).

It appears, therefore, that Stanton's results are explicable, if it is assumed that the v^2 law breaks down for small Pitot-tubes.

Investigation Undertaken in Present Paper.

In view of the results discussed above, it seemed of interest to examine the pressure differences between a Pitot and static-tube when placed in a fluid moving with very low velocity.   It seemed probable that, for values of the velocity less than a certain fixed value, the pressure differences would cease to vary as the square of the speed.   The present investigation was under-

taken with a view to determining this region, and, should sufficiently accurate measurements be possible, to determining the relation between pressure difference and velocity in this region.

A Pitot-tube of circular cross-section was mounted in the centre of a pipe through which water, in a state of stream-line motion, was flowing. A hole in the side of the pipe opposite the mouth of the Pitot-tube was connected to one side of a manometer and the Pitot to the other. The pressure differences registered by the manometer for various values of the mean velocity, down to as low a velocity as possible, were observed.

Since the velocity at the centre of a pipe, through which water is flowing in stream-line motion, is equal to twice the velocity of mean flow, the velocity at the centre of the pipe was found by measuring the volume of water ejected from the pipe in a given time.

Results and Conclusions.

As a result of the investigation, it is found that the law $p = \frac{1}{2}\rho v^2$ holds down to a velocity at the centre of the pipe of 6 cm. per second, *i.e.*, for values of $rv/\nu > 30$, where r is the radius of the Pitot-opening, ν the kinematical viscosity of the fluid, and v the velocity of the fluid at the centre of the Pitot-opening.

For values of $v < 6$ cm. per second, the pressure differences are greater than would be given by the above law, and we have a definite indication (see fig. 2) of a viscosity effect.

It was surmised that this viscosity effect might show itself in the form of an additional pressure, comparable with that at the nose of a sphere of radius equal to that of the Pitot opening, when placed in a stream moving with a velocity equal to that at the centre of the pipe. If this pressure be denoted by p_1, we have, as before (see Introduction),

$$p_1 = \frac{3}{2}\frac{\mu v}{r}.$$

The results, in fact, give support to such a supposition. For, from the mean curve of fig. 2, we can determine the experimental values of the pressure differences for values of $v < 6$ cm. per second. Now, if we plot these experimental values against values of the pressure obtained from the formula

$$p = \frac{1}{2}\rho v^2 + p_1 = \frac{1}{2}\rho v^2 + \frac{3}{2}\frac{\mu v}{r},$$

the points are found to lie on a straight line through the origin (see Table II and fig. 3). The accuracy with which the points lie on this line is
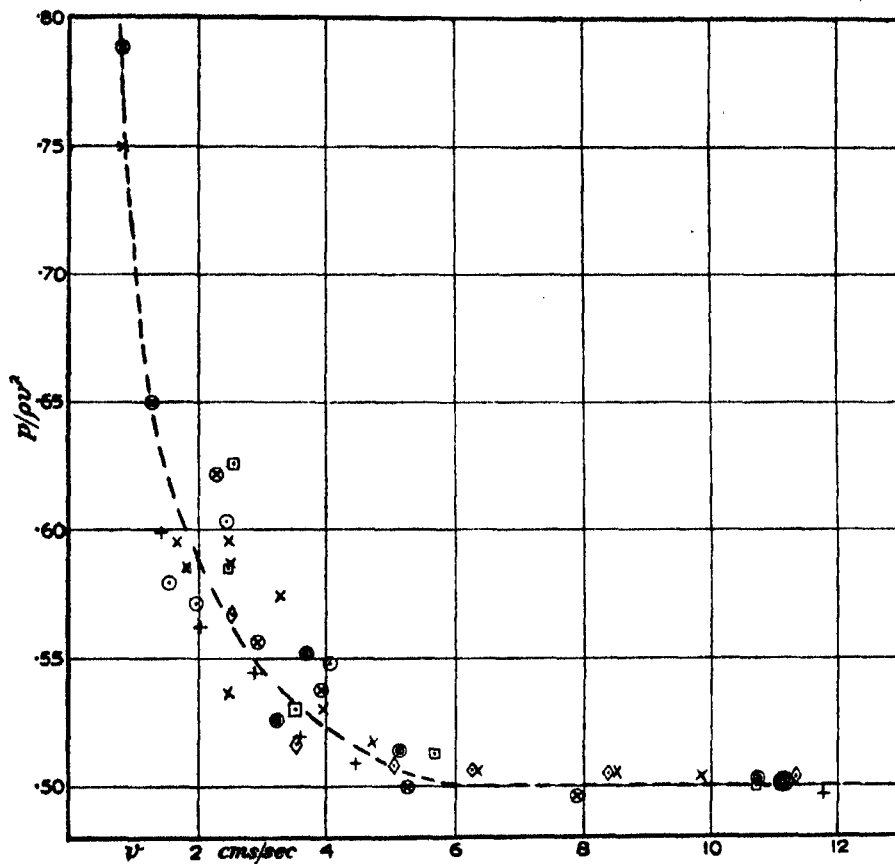
Fig. 2.

v = velocity at centre of pipe = twice mean velocity of outflow.
p = pressure difference between Pitot and static tubes.
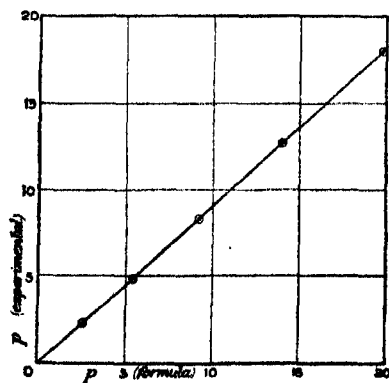Different symbols indicate different sets of readings (see Table I).

Fig. 3.

Ordinates mean of fig. 2. Abscissae from formula.

probably fortuitous, but a viscosity effect of the type suggested is clearly demonstrated.

It is interesting to note that much of Stanton's work is carried out in a

Table I.

v = velocity at centre of pipe = twice mean velocity of outflow.

p = pressure difference between Pitot and static-tubes.

(For use of symbol attached to each set of readings in Column T, see fig. 2.)

T.	v cm. per sec.	p dynes per sq. cm.	$p/\rho v^2$.	T.	v cm. per sec.	p dynes per sq. cm	$p/\rho v^2$.
° C. 13	0·82	0·53	0·788	° C. 14·6	2·42	3·42	0·585
	1·35	1·19	0·650		2·55	4·08	0·626
	2·35	3·43	0·622		3·52	6·59	0·530
	3·12	5·41	0·557		5·67	16·50	0·513
	3·96	8·44	0·538	▫	10·65	58·80	0·500
	5·24	18·70	0·500				
	7·90	30·75	0·494	15	0·84	0·53	0·750
⊗	11·14	62·10	0·500		1·70	1·72	0·595
					1·84	1·98	0·585
14	2·51	3·56	0·568		2·44	3·56	0·596
	3·58	7·25	0·566		2·46	3·80	0·546
	5·09	13·19	0·509		2·51	3·70	0·587
	6·23	19·65	0·506		3·32	6·33	0·575
	8·38	35·50	0·505		3·96	8·30	0·530
◇	11·34	64·90	0·504		4·74	11·60	0·517
					6·34	20·30	0·506
					8·42	35·90	0·506
14	1·58	1·15	0·580		9·87	49·30	0·504
	1·95	2·175	0·572	×	11·11	62·00	0·502
	2·45	3·625	0·604				
	4·07	9·10	0·549	15	1·41	1·19	0·598
⊙	11·12	62·00	0·500		2·05	2·375	0·565
					2·87	4·48	0·545
14·2	3·21	5·41	0·526		3·60	6·725	0·520
	3·695	7·52	0·552		4·44	10·01	0·509
	5·15	13·60	0·514	+	11·76	68·75	0·496
◎	10·73	58·05	0·503				

TABLE II.

Experimental values of p from mean curve of fig. 2.

Theoretical values of p given by $p = \frac{1}{2}\rho v^2 + \frac{3}{2}\mu v/r$.

v cm./sec.	p exper.	p theor.
2	2·35	2·6
3	4·9	5·4
4	8·4	9·2
5	12·7	14·0
6	18·0	19·8

region for which $rv/\nu < 30$, where in this case $2r$ is taken to be the breadth of the rectangular Pitot-tube.

For example, taking No. 3 Pitot and the case when $r = 0.0064$ cm. and $v = 400$ cm. per second, we have

$$rv/\nu = 20 \text{ approx.}$$

Description of the Experiment.

A brass pipe, some 70 cm. long and 1·1 cm. diameter, was fitted with a small Pitot-tube whose cross-section was 0·1 cm. in diameter, and whose axis coincided as nearly as possible with the axis of the pipe. This tube was connected to one side of a Chattock tilting gauge. Slightly behind the mouth of the Pitot-tube, a hole in the side of the pipe was connected to the other side of the gauge (see fig. 4).

As water was the fluid flowing through the pipe and contained in
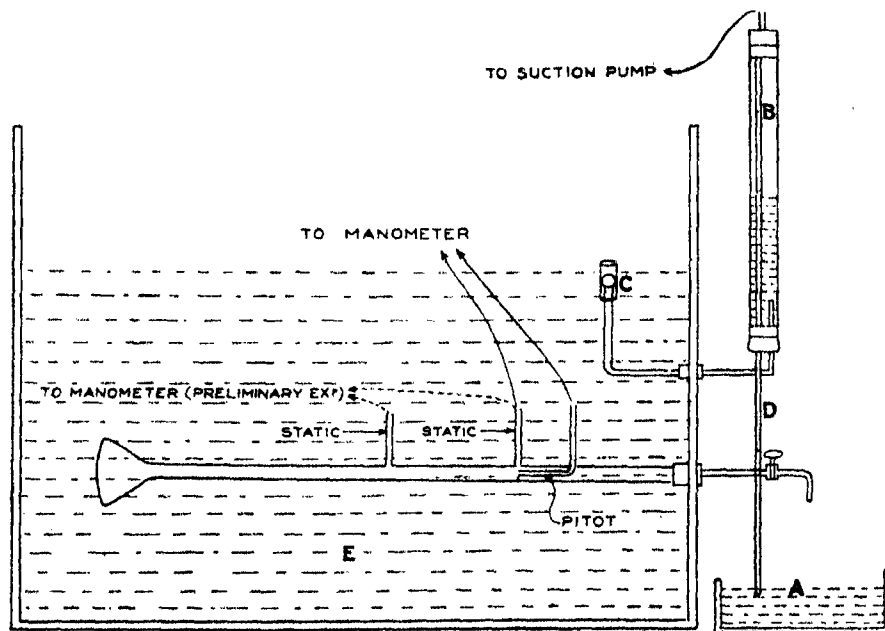
Fig. 4.—Diagram of apparatus. Not to scale.

the connecting tubes and upper halves of the manometer bulbs, brine could not be used as the heavy liquid in the manometer. Instead, nitro-benzene, of density 1·207, was used, and, as the difference in density between the two liquids in the manometer bulbs was now only 0·207, the sensitivity of the manometer was increased about five times, and was such that one

division of the circular scale represented a pressure difference between the two sides of 0·00134 mm. of water.

The pipe was provided with a smooth converging mouthpiece and placed in a trough of water, E, the level of which was kept constant by means of a circulating pump.   The end of the pipe projected through the side of the trough, and was provided with a stop-cock, by means of which the flow could be regulated.   The water from the pipe was received in a trough, A, from which it was withdrawn by means of a suction pump up a long tube, D, into a thin glass cylinder, B.   As soon as the water in A fell below the mouth of the tube D, the pressure of the water that had been drawn up into B opened the steel ball-valve at C, and the water in B flowed back into the trough E.

With this method of circulating the water, it was found ·that, though the temperature of the water in the trough varied from day to day, it remained reasonably constant over the period of 2–3 hours needed to take a set of readings.   The water was allowed to circulate for some time before readings were taken, and a record of the temperature was kept.

Preliminary Experiment.

As a preliminary experiment, the pressure differences between the static-tube and a second static-tube nearer the mouth of the pipe were measured for different rates of mean flow, in order that the critical velocity for the pipe might be determined.

In the tabulated results (see Table III) the pressures have been corrected *for temperature in accordance with the laws of dynamical similarity.*   The results are illustrated in fig. 5.   It will be seen that, for velocities at the centre of the pipe of less than 12 cm. per second, the velocity is proportional to the pressure differences, and hence stream-line motion exists in this region.   The principal experiment was therefore carried out in this region.

Principal Experiment.

The Pitot-tube and the static-tube opposite its mouth were now connected to the two sides of the manometer, and a series of readings taken for velocities varying from 12 to 0·8 cm. per second.   The water ejected from the pipe in a certain time, determined by a stop-watch, was weighed. In the manometer used, one revolution of the wheel corresponded to a pressure difference of 0·0648 cm. of water.   The circular scale on the wheel was divided into hundredths, and readings could be depended upon to one division.   The difference of density between the two liquids in the
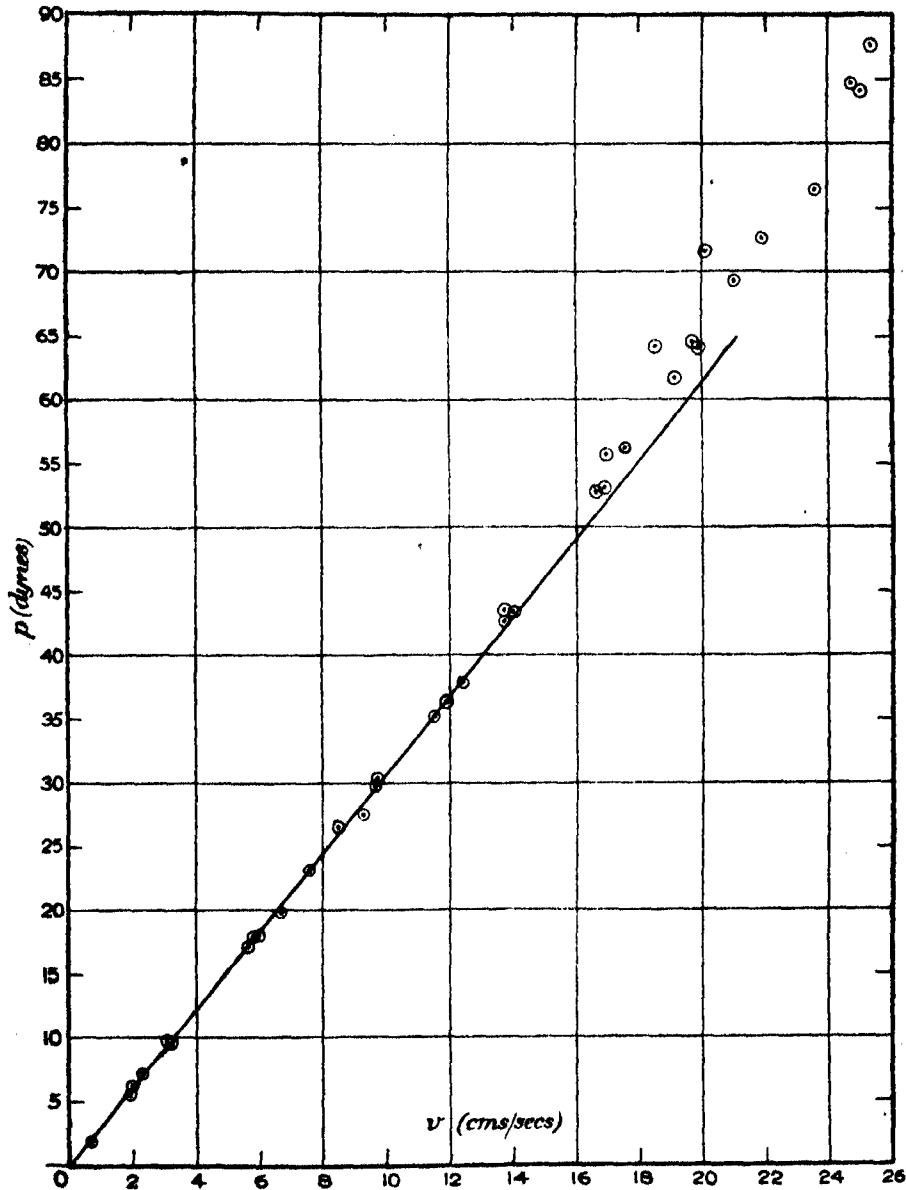
Fig. 5.
v = velocity at centre of pipe = twice mean velocity of outflow.
p = pressure difference for a length 18·5 cm. of pipe at 12° C.

manometer bulbs was 0·2072. Thus, given a reading *h* in revs. of the manometer wheel, the pressure *p* in dynes was given by the formula

$$p = 0.2072 \times g \times 0.0648h = 13.17h.$$

Table III.

v = velocity at centre of pipe = twice mean velocity of outflow.
p = pressure difference for a length 18·5 cm. of pipe at 12° C. (the pressures have been corrected for temperature).

v cm. per sec.	p dynes per sq. cm.	v cm. per sec.	p dynes per sq. cm.
1·87	5·7	16·78	55·7
3·22	9·6	18·52	64·1
6·66	19·8	20·10	71·6
11·94	36·4	20·80	69·2
15·16	47·4		
16·60	52·8	2·30	7·2
19·12	61·6	5·60	17·1
19·88	64·1	9·69	29·9
24·70	84·8	12·40	38·0
		17·57	56·1
5·80	17·9	21·05	69·4
8·47	26·5	25·00	84·1
13·70	42·7		
19·70	64·6	0·69	1·8
21·95	72·6	2·00	6·3
25·40	87·8	3·12	9·75
		5·85	18·1
1·93	5·75	7·60	23·1
6·00	18·0	9·24	27·6
9·80	30·4	11·50	35·2
13·69	48·5	16·84	53·1
14·00	48·3	28·62	76·5

Discussion of the Results.

The results are tabulated in Table I and illustrated in fig. 2 above, where $p/\rho v^2$ is plotted against velocity, and we obtain a mean curve of the usual " scale effect " type. From the fact that, down to so low a velocity as 6 cm. per second, the experimental points lie so consistently on the line $p/\rho v^2 = \frac{1}{2}$, we see that the pressure difference between the Pitot and static-tubes used in the experiment does give a very accurate measure of the square of the velocity for values of $v > 6$ cm. per second. The results obtained for values of $v < 6$ cm. per second give a very definite indication of a viscosity effect on the relation between p and v in this region.

It will be seen from Table I that, with decrease of v, the pressure differences registered by the manometer become exceedingly small. The degree of approximation obtained can be estimated from the distribution of the points in the figure.

For different sets of readings, the temperature of the water varied from 13° to 15° C., and this variation would be expected to influence the results in the region just mentioned. But the pressure differences were too small for any effect to be detected.

It seems probable that more accurate data for this purpose could be obtained by repeating the experiment, using, instead of water in the pipe, a liquid of, say, five times the density of water. Then, according to the laws of dynamical similarity, the viscosity effect should show itself over a range of velocities for which accurate results could be obtained.

In conclusion, I should like to express my hearty thanks to Mr. G. I. Taylor, F.R.S., at whose suggestion the experiment was undertaken, and to whom I am indebted for much valuable help and advice during the course of the work.

On the Susceptibility of Feebly Magnetic Bodies as Affected by Compression.

By Ernest Wilson, M.Inst.C.E., M.I.E.E., Siemens Professor of Electrical Engineering in the University of London.

Introduction.

This communication undertakes an investigation of the complex problem which is presented by the effects of mechanical stress upon the susceptibility, retentivity and other properties of magnetic substances. The present experiments are confined to compressive stress, and its effects upon the susceptibility of certain rock specimens. It was felt that an investigation into this part of the subject might possibly throw some light upon the susceptibility of the earth's crust as affected by the enormous forces with which it has to contend, and their variations. It is unfortunate that, owing to the nature of rock specimens, the compressive stress has been limited to about 1200 kgrm. per square centimetre, but, nevertheless, some interesting results have been obtained, and these are recorded in the present paper.

All the specimens are in the form of short bars about 4 cm. in length, whose cross-section is either square, being 1 cm. across each side, or 1 cm. in diameter; and, throughout the work, the compressive stress has been applied in the direction coinciding with the length of the bar. The susceptibility has been measured (*a*) in the direction of the stress and (*b*) at right angles thereto.

Susceptibility Measured in the Direction of Stress.

The apparatus consisted of a horizontal wrought iron lever pivoted at one end; the effective length of the lever was 90 cm. The specimen to be tested was placed vertically in line with two stalloy plungers, whose cross-section was square and measured 1 cm. across each side. The horizontal distance between the centre line of the specimen and the fulcrum was 5 cm., and the compressive force acting on the specimen, due to a weight hung from the end of the lever, was therefore increased 18 fold. In the calculations due allowance was made for the weight of the lever itself.

A stalloy yoke was used to magnetise the specimen, and consisted of nine stampings of ring-form; the thickness of each was 0·32 cm., the internal diameter was 7·62 cm., and the external diameter was 12·7 cm. Each stamping had an air-space 2 cm. wide, with its sides parallel to a diameter, and the plane of the stampings was at right angles to the lever. The three central stampings, with two additional thin ones to make up the required thickness of 1 cm., were cut in a direction at right angles to the parallel sides of the gap, to accommodate the plungers and test-piece. In order that the magnetic circuit should not be disturbed any more than possible, the plungers were screwed on to gunmetal pieces fixed respectively to the lever and base of the apparatus. By this method it was possible to vary the longitudinal compressive force, and to magnetise the specimen to varying degrees by the passage of an electric current through the magnetising coil wound on the yoke. This coil consisted of four layers of copper wire 0·061 cm. in diameter (No. 23 S.W.G.), doubly insulated with cotton. The turns per layer were, from innermost to outermost, 131, 128, 118, 112, giving a total of 489, and experiment showed that the magnetising force H in the gap per ampère of magnetising current was very closely 352 C.G.S. units.

A secondary circuit consisting of 120 turns of fine silk-covered copper wire of resistance 4 ohms, was wound on a square cardboard former which allowed of the insertion of the test-piece, and allowance was made for the non-magnetic space occupied by the former. This coil was connected to a ballistic galvanometer, and a resistance box was included in the circuit. Deflections were observed on reversal of the current in the magnetising coil: firstly, when the test-piece was in position; and, secondly, when the test-piece was replaced by a wooden core of the same dimensions. Allowing for the alteration in resistance, when necessary, the permeability μ has been taken to be the ratio of the deflections. The volume-susceptibility K_v was then calculated from the formula $\mu = 1 + 4\pi K_v$.

Preliminary tests were made with a brass test-piece to discover if com-

pressive forces, equal to the maximum forces used in the experiments, had any effect upon the deflections. It was found that, on reversal of the same magnetising current, the ballistic deflections were uninfluenced by the application of the compressive stress.

Longitudinal Susceptibility.

The specimens of magnetite chosen for these experiments exhibit widely different characteristics, and the variations in their normal magnetic properties, as exhibited by crystallised, compact, or massive specimens and detached particles, have been already studied.[*]

New York State : Density 4·86.—This variety of magnetite is very uniform, hard and compact, with no indication of cleavage planes. It has a bright, irregular fracture, with many glistening points. It is characterised by a high maximum susceptibility (1·64), which occurs at a relatively small value of the magnetic force (30·6), and in these respects comes next to the magnetite (Traversella) crystal. It has a small coercive force (16·8), and its permanent magnetisation is small. A specimen of this magnetite has been subjected to longitudinal compressive stress up to 1250 kgrm. per square centimetre, and the curves given in fig. 1 show the variation in volume susceptibility. Each

Fɪɢ. 1.
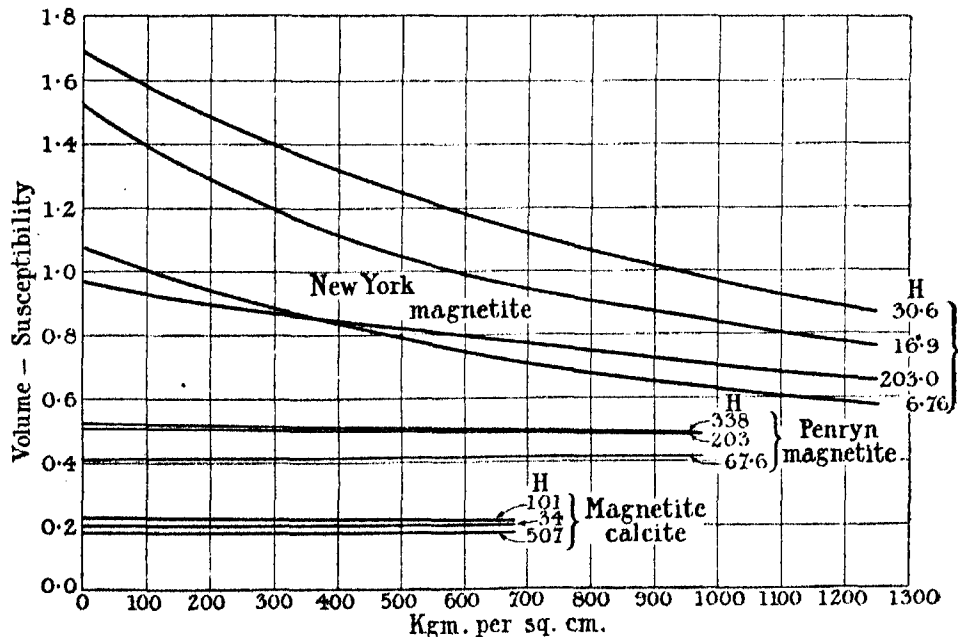
[*] ʻProc. Phys. Soc.,ʼ vol. 31, Part V, August 15, p. 299 (1919).

curve corresponds to a given magnetic force H which is indicated in the diagram. The diminution in susceptibility, due to the increase in compressive stress, is very marked, its value under a magnetic force ranging from 6·76 to 30·6 C.G.S. units being halved in magnitude when the compressive stress was equal to 1250 kgrm. per square centimetre. It is noticeable that the gradient is less when a magnetic force of 203 is employed. On removal of the compressive force, the susceptibility returned to its initial value. The experiments do not show what would be the effect of further increase of the compressive force as the specimen was crushed on the application of 1540 kgrm. per square centimetre.

Hey Tor, Devon : Density 4·30.—This variety exhibits a great irregularity in the distribution of magnetite, and consists of minute crystals mixed with earthy material. The fracture has some sparkling points due to the small crystals, but otherwise it is dull and earthy. Its maximum susceptibility (0·90) is relatively high, coming next to the New York specimen, and it occurs at a higher value of the magnetic force (33·8). The curves in fig. 2 for forces in the neighbourhood of those at which maximum susceptibility occurs, indicate a considerable diminution in susceptibility, as the compressive stress is increased up to about 500 kgrm. per square centimetre. Under a force H = 16·9, the susceptibility was, in fact, reduced 35 per cent., and from the trend of the curve, the reduction might have been greater than in the New York specimen for the same ultimate pressure. The application of 675 kgrm. per square centimetre unfortunately crushed the specimen. When the magnetic force is either small (6·76) or large (338) the variation of susceptibility with pressure is reduced, but it is still considerable at the lower force.

Penryn, Cornwall : Density 4·59.—This variety of magnetite is hard and strong, with dull fracture. It contains small inclusions of a red-brown softer substance, which were found to be mainly ferric oxide and ferrous carbonate, but otherwise compact. Its maximum susceptibility (0·51) occurs at a high value of the magnetic force (338) and is not very pronounced. It will be seen on inspecting fig. 1 that a compressive longitudinal force of 1000 kgrm. per square centimetre has had little effect upon susceptibility when the magnetic force H varied from 68 to 338 C.G.S. units.

The method of test does not allow of an accurate determination of susceptibility at various temperatures, but in order to obtain some idea as to the effect of heating, a coil of platinum wire 0·05 cm. diameter, after being insulated with asbestos paper, was wound around the specimen. It served as a heating coil, and also as a secondary coil for use with the ballistic galvanometer. A platino-iridium junction placed close to the specimen indicated the surface

temperature during a test made with variation of the compressive force. With a pressure of 961 kgrm. per square centimetre, and a magnetic force H = 338
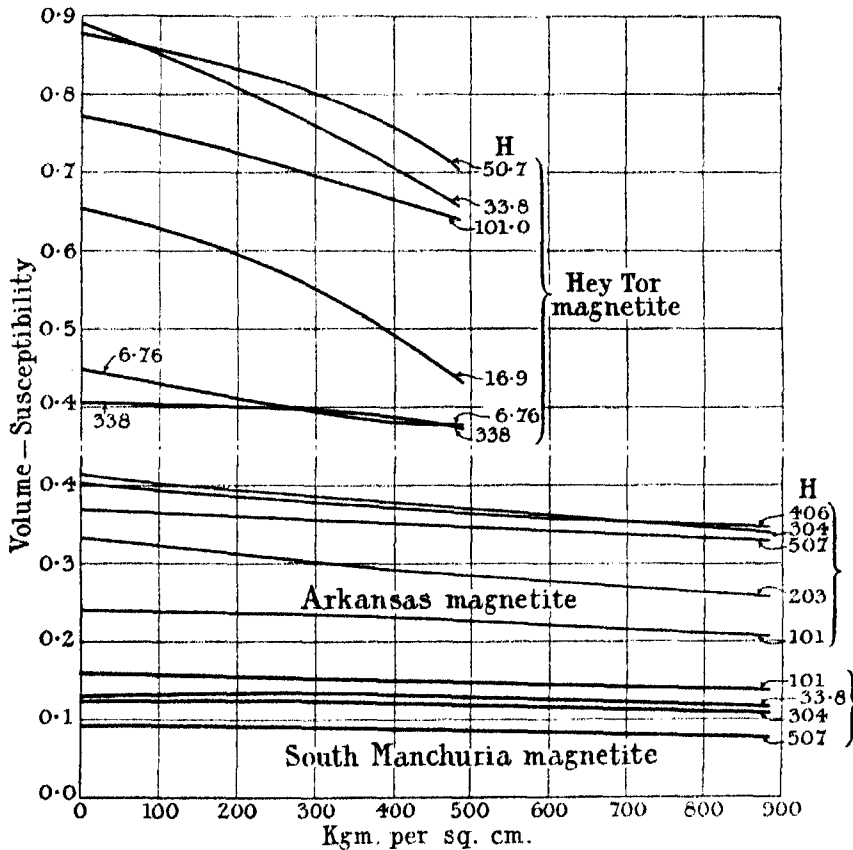

Fig. 2.

constantly applied, the magnetic induction B was halved in value as the indicated temperature increased from about 100° C. to 450° C. In the case of the New York specimen a similar heating test was carried out, and with a compressive stress equal to 1250 kgrm. per square centimetre the susceptibility was found to fall with increasing temperature when the magnetic force had the value 203, whereas it increased when the magnetic force had the value 30·6. This is in agreement with what happens in the case of iron. The maximum recorded temperature was about 350° C. in this case.

Arkansas : Density 4·74.—This kind of magnetite consists of a hard compact material with irregular cleavage planes, and almost vitreous fracture in some directions, whilst in others it exhibited a silky lustre. It has a well pronounced maximum susceptibility (0·41), which occurs at a force H of

about 300 C.G.S. units. It will be seen from the curves in fig. 2 that the gradient in the susceptibility, when plotted in terms of the compressive force, was small, though not so small as in the case of the last variety, in which the maximum susceptibility was not so pronounced. As this magnetite has a high coercive force and great retentivity, experiments were made to discover what effect compressive stress might have upon these quantities. At about 900 kgrm. per square centimetre the coercive force was 138 C.G.S. units, whereas it was 154 with no pressure. Similarly the retained magnetic induction was reduced from 1150 to 823 C.G.S. units on application of the above pressure. The maximum value of the magnetic force in this test was 507 C.G.S. units.

South Manchuria : Density 3·40.—This variety is essentially a schist with slaty cleavage, and has the lowest susceptibility (0·16) of any rock which can be termed a magnetite. The specimen broke down along a cleavage plane which was parallel to its length and to the direction of the stress when the kilogrammes per square centimetre exceeded about 900. The curves in fig. 2 show that compressive stress up to about 900 kgrm. per square centimetre has little or no effect upon susceptibility at magnetic forces ranging from 100 to 500 C.G.S. units.

Magnetite Calcite : Density 3·40.—This rock cannot strictly be classed as a true magnetite. It consists of very small crystals or crystalline grains of magnetite in a matrix of calcite. The maximum susceptibility of the tested specimen has the value 0·23 when the magnetic force is about 100, and as shown by the curves in fig. 1 there is a small diminution due to the application of compressive stress, which had to be limited to about 700 kgrm. per square centimetre. The specimen began to crush on the application of greater pressure.

Altered Carbonate (Bettwys Garmon).—By its appearance this rock might be mistaken for a magnetite, but it cannot be classed as such. The compressive stress was increased by stages to 887 kgrm. per square centimetre, and the susceptibility was reduced from 0·0876 to 0·0796, the magnetic force H being 304. The susceptibility at any of the applied pressures was slightly greater in the neighbourhood of $H = 300$ to 400 than at higher or lower forces.

Susceptibility measured at Right Angles to the Direction of Stress.

The method of observing the effect upon susceptibility of compression at right angles to the applied magnetic field is strictly limited in its higher range to values of the susceptibility of about 0·1, on account of the demagnetising effect due to the specimen. It involves the measurement of

the force of attraction exerted by the specimen upon a permanent hard steel magnet suspended from one end of the beam of a special form of balance.* The compressive stress was produced by a lever arrangement substantially as described, except that gun-metal was employed throughout. The specimens were approximately circular in section and 1 cm. in diameter. The results of the tests which were of a somewhat qualitative nature are summarised in the subjoined Table:—

Mineral.	Volume-susceptibility (normal).	Maximum compressive stress.	Magnetic force during test.	Remarks on susceptibility variation.
		kgrm. per sq. cm.		
Magnetite (New York State).........	1·64 (max.).	263	12	No alteration observed.
Magnetite (Penryn)	0·51 ,,	250	12	No alteration observed.
Pisolitic iron ore traces† (Dolgelly)	0·014	848	16	About 8 per cent. increase.
Dolerites—*†				
(a) Whitwick, Leicestershire	0·004	286	51	About 10 per cent. increase.
(b) Owthorpe, Nottinghamshire....	0·0047	390	51	Very small increase.
(c) Southwell, Nottinghamshire...	0·0021	218	16	Very small increase.
Granite*† (Mount Sorrel, Leicestershire)	0·0018	250	51	No alteration observed.

* 'Phil. Trans.,' A, vol. 219 (Appendix) (1919).
† 'Roy. Soc. Proc.,' A, vol. 96, p. 429 (1920).

Conclusions.

1. *Susceptibility measured in the Direction of Compressive Stress.*—Rock specimens, in the form of short bars, have been subjected to compressive stress whose direction coincides with the length of the bar, the maximum value of the stress varying from 900 to 1250 kgrm. per square centimetre, except in one or two cases when the specimen gave way under the pressure. It is found that in certain varieties of magnetite in which the susceptibility reaches a pronounced maximum value, the diminution of susceptibility with increase of pressure may be of the order 50 per cent. under magnetic forces in the neighbourhood of, and including, those at which the maximum susceptibility occurs. The gradient is less under magnetic forces whose values are either very much larger or smaller than the above. The retained magnetic induction and coercive-force are also reduced by pressure. In the case of rock specimens whose maximum susceptibility is not

* 'Roy. Soc. Proc.,' A, vol. 98, p. 274 (1920).

pronounced the gradient is less, and in extreme cases is practically non-existent.

2. *Susceptibility measured at Right Angles to the Direction of the Compressive Force.*—Rock specimens whose normal susceptibility varies from 1·6 to 0·0016 have been tested at pressures varying from 250 to 390 kgrm. per square centimetre.   In all cases in which a variation has occurred it has been to slightly increase susceptibility with increase in pressure.

The Properties and Molecular Structure of Thin Films.
Part II.—Condensed Films.

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(Communicated by W. B. Hardy, Sec.R.S.   Received May 4, 1922.)

CONTENTS.

1. *General Structure of the Films.*

In this and a following paper, an account will be given of work done in continuation of the experiments on thin films of palmitic acid, described in Part I of this investigation (1), and, in particular, of the results obtained by extending the range of substances composing the films, and the range of temperature over which the experiments were made.   As was there pointed out, the study of these films is a peculiarly attractive one, owing to the extremely simple manner in which the molecules are arranged; the films

being of one molecule in thickness and the molecules in them being arranged not indiscriminately, but perpendicular to the surface and parallel to each other, as a rule. The experimental method (due in principle to Langmuir) has also a great advantage over those more commonly employed in capillary studies, that the forces tangential to the surface are measured directly. Exceptionally direct information is therefore obtainable as to some of the forces between the molecules composing the films, and by a study of the influence of chemical constitution on the properties of the films, much light should be shed upon the important problem of the relation between chemical and capillary forces.

It will not be necessary to occupy space in proving that, for any of the substances here studied, the films are one molecule in thickness. Reasons for taking this view have been given by other workers, as well as on p. 344 of my preceding paper, and it is sufficient to say that the experiments described here afford evidence of the same character, which is equally conclusive for each one of the substances investigated.

The general arrangement of the experiment has been as before, and is shown in the drawing (fig. 1). Some points of detail to which attention is necessary in conducting experiments are noted in Section 15. It is desirable, however, before proceeding to the discussion of the results obtained, to make clear what is the interpretation which will be adopted of the forces acting on the balance float which bounds one end of the film.

Previous to putting on the film, the surface is cleaned by means of the barrier CD, sweeping away all contamination to the left. A clean surface possesses the property that *CD* may be moved *right up to the float AB* without any repulsion occurring before contact. In practice, this degree of cleanliness has been very nearly approached. A known quantity of the substance under examination is immediately put on, dissolved in a volatile solvent, which first serves to spread it in a uniform film over the whole of the available surface, and then evaporates in a few seconds. It is found that the film remaining will transmit a force of repulsion from the glass barrier to the float, and that the film possesses a definite area at a given force. The curves called " compression curves " exhibit the force on the float AB in dynes per centimetre as ordinates, and the areas per molecule in the film as abscissæ. The areas will be expressed in terms of the unit 10^{-16} sq. cm., which will be denoted by Å.U., following Sir W. H. Bragg (2).

This force will be regarded simply as a force of compression acting on the film; the film, *as a whole*, and any other floating objects, being considered as not subject to any tangential forces whatever by the water. The film of molecular thickness covering a portion of the surface will be regarded in much

Fig l.

the same way as any other body floating on the surface. Force transmitted from the barrier CD to the float AB is conveyed as a thrust in the floating film. A perfectly simple picture is obtained in this way of the part played by each molecule in the film, and the forces acting upon it. Each one is attracted strongly to the water, particularly by the polar group directed towards it; the hydrocarbon chains, which are arranged more or less perpendicular to the surface, exert a lateral attraction upon each other, and these two sets of forces appear to be the principal factors in determining the stability of the film. They are so powerful that the film will resist, without serious deformation in many cases, very considerable forces of compression laterally; it will be evident presently from the diagrams that forces of over 45 dynes per centimetre are occasionally withstood before buckling takes place, and this, calculating from the thickness of the films, is over 200 atmospheres. Finally, the observed force of repulsion on the float AB is the direct result of all the inter-molecular forces of repulsion acting between the individual film molecules, and therefore the area of the films under a given compression affords direct evidence as to the cross section of those parts of the molecules which are in contact. It will appear, later, that there is much evidence that many of the molecules studied, though their general shape is highly elongated, have not the same cross-section at all points of their length; and an attempt has been made to estimate the maximum cross-section of many of the polar groups, which appear as a rule to be somewhat wider than the hydrocarbon chains.

While in the preceding paper, over the limited range of temperature studied, it appeared correct to consider the films as composed of molecules in direct contact with one another over the whole area, and therefore the thermal movements among the molecules could be to a large extent neglected, just as can the vibrations of the atoms composing a crystal, in the discussion of their general arrangement in the second of these two papers it will become necessary to take account of these thermal movements. In every one of about twenty substances studied, when the temperature of experiment was sufficiently high, a definite change took place in the properties of the film, resulting in a considerable increase in the space occupied per molecule. This change was identical with that previously described by Labrouste (3), and the further study to be described in Part III has shown that its principal features were the same for all the molecules investigated, which had only one feature in common, namely, a hydrocarbon chain of 12 to 22 carbon atoms in length. This change appears almost certainly to be a separation of the molecules from one another in the surface, brought about by the thermal agitation becoming so violent that the lateral attractions of the molecules for each other (already

referred to as one of the main stabilising forces in the films) are overcome. The films in this state will be designated " expanded films "; their properties in many respects are those of a gas, or rather vapour, in two dimensions; and at temperatures close to that at which the expansion takes place, transitional phenomena are observed analogous to those attending the passage from the liquid to the vapour state; the isothermals (connecting, of course, compression and area) closely resembling the isothermals of a vapour near the critical point. It has been mentioned that the main features of the expansion are ·the same for all the films studied; it will appear later that there are important differences in detail which can, on the one hand, be certainly correlated with the length of the hydrocarbon chains, and therefore with the magnitude of the attractive forces between the individual film molecules; and, on the other, very probably, with the magnitude and nature of the forces exerted by the molecules of the underlying solution (or water) on the parts of the film molecules in most immediate contact with them, and thus probably with the forces which are operative between solute and solvent molecules in a solution. Those films in which the molecules appear to be in direct contact over the whole area will be designated " condensed films."
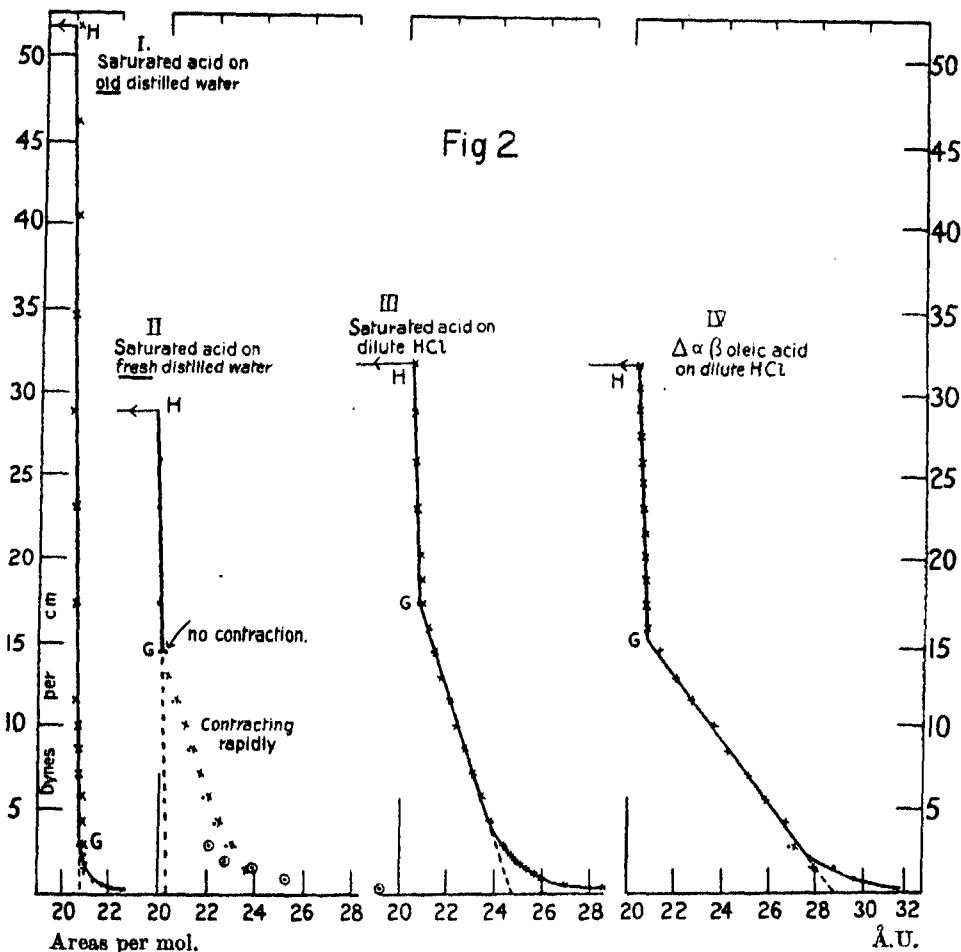
In figs. 2 to 4 are given the compression curves of the substances which have been investigated most fully up to the present; all these curves are (as will be shown) to be regarded as those of condensed films.

2. *The Fatty Acids on Distilled Water.*

Fig. 2 is of substances which contain the free COOH group, and the curves I and III are identical with the curves given in my preceding paper, determined on palmitic acid only. They are reproduced here, as their form has now been determined at compressions lower than the lowest previously recorded, and also because many more experiments have shown that the slope previously given was not quite steep enough.

Curve I is what was obtained on distilled water *which had been in the trough several days.* It was found to be exactly the same for the following acids;

Fig 2

I.
Saturated acid on
<u>old</u> distilled water

II
Saturated acid on
<u>fresh</u> distilled water

III
Saturated acid on
dilute HCl

IV
Δ α β oleic acid
on dilute HCl

no contraction.

Contracting
rapidly

Dynes per cm

Areas per mol.

20 22   20 22 24 26 28   20 22 24 26 28 20 22 24 26 28 30 32

Å.U.

myristic, pentadecylic, palmitic, margaric, stearic, heneicosoic, and behenic (the saturated acids C_{14} to C_{22} with the exception of C_{19} and C_{20} which were not available), and for the isomer of oleic acid which has the double linkage between the α- and β-carbon atoms. The phenomena presented by the commoner unsaturated acids, which have the double bond in the middle of the chain, have not yet been sufficiently worked out, but it may be said that under certain circumstances some of them give a compression curve which closely resembles this one, and I am now doubtful whether the conclusion drawn by Langmuir and accepted by me (4), that these acids form films in which the double bond itself occupies a definite area on the water, providing

a second point of attachment for the molecule, will prove to be capable of explaining the phenomena.

Three other saturated acids were tried, lauric (C_{12}), tridecylic (C_{13}), and cerotic (C_{26}). The first two gave results approximating to the same curve as the other acids, but complicated by the steady shrinkage of the films through solution of the molecules in the water. The best specimen of cerotic acid which I could obtain gave a film which did not spread properly in benzene solution on the surface, and the film showed a constant tendency to contract, with the appearance of the aggregates characteristic of the collapse of a mono-molecular film of the lower acids when the compression is high enough to buckle the film. It may be that the specimen was not pure enough, or perhaps the chains are so long that their lateral attraction for one another is sufficient to drag the molecules away from the water, into the aggregates, spontaneously. The area per molecule was, however, roughly the same as that of the other acids of the series.

It will be noticed on close inspection that the curve is not quite straight. The line drawn is straight, and the points lie somewhat to the right of it at the top and at the bottom, showing that the compressibility decreases slightly at higher compressions. It is always however very small, and comparable with the compressibility of liquid paraffin in bulk, as was previously shown. The figure given in the previous paper for the compressibility was too great; the apparatus is not of course suited for accurate measurements of such small compressibilities, and it must be remembered that any error such as undetected leakage past the barriers, or slight collapse of the monomolecular film locally will increase the observed compressibility, so that in estimating the order of magnitude preference should be given to low values. The earlier value was 1·7 per cent. decrease in area for 10 dynes per centimetre. This has since been found to be exceptionally high for a good experiment. Usually it is about 0·8 per cent., and in some instances, on chains of 18 carbon atoms and upwards in length, values as low as 0·4 per cent. have been found. The earlier value recorded was about five times the volume compressibility of $C_{15}H_{32}$ so that the later observations show the true compressibility in this portion of the curves to be nearly the same as that of this liquid in bulk.

3. *Cross Section of a Hydrocarbon Chain.*

Though the very nearly straight line GH in fig. 2, curve I, is nowhere duplicated in its full length, parts of it are very common in the upper portions of the compression curves of condensed films. It has been found in all those given here, except with stearic nitrile and the substituted ureas below a transition temperature which will be later noted. Once the state corre-

sponding to GH has been attained, it continues as the compression is increased until collapse at H takes place. Produced to meet the line of no compression, this curve cuts it at 21·0 Å.U. This figure is the mean of a large number of experiments on twenty different substances, all the observations being between 19 and 23, and the majority between 20 and 22 Å.U. I have included in some of the curves the points corresponding to typical duplicate experiments, in order to give an idea of the accuracy which is obtainable when working with the greatest care. There is usually rather more error in knowing the amount of material put on than in determining the relative areas under different compressions, as is shown by the fact that the points not on the curves in fig. 3, I and III, lie on curves parallel to those drawn in. Different experiments are indicated in the diagrams by different kinds of points.

The area of the intersection 21·0 A.U. is probably correct within a few decimals, unless there is any constant error in the experiments. Two possible sources of such error should be discussed. In the previous paper a correction was applied for the residual contamination left after cleaning the surface before putting on the film, by determining approximately its amount before putting on the film and subtracting the area it occupied from the observed area of the film. Probably the amount subtracted was too great, perhaps much too great, since it has been found extremely difficult in later work to detect any difference between uncorrected curves determined on surfaces on which there was not more than 2–3 mm. of residual contamination at 1·4 dynes per centimetre, and where five times this quantity was present. If the correction were correct one would have expected a difference in area at about 5 dynes per centimetre of about 0·5 unit, and the determinations of the area of intersection might be on the average about 0·3 unit too great, taking a liberal estimate of the average amount of contamination which has remained on the surfaces in this series of experiments. But since the correction is probably a good deal too high, it is unlikely that residual contamination has made the determination of this average value as much as 0·2 Å.U. too great.

The influence of the air blasts at the ends of the float AB (fig. 1) might also have made the observed area slightly too great by blowing the film away from the barrier, so that what was really a bare patch was taken as covered by the film. The amount of error from this cause was probably very small indeed. It was impossible to see directly how far the film was blown back; but when a solid film such as tripalmitin was put on, and talc sprinkled on the surface, the area in which the solid structure was destroyed could be seen. It did not amount to more than a correction of about 0·2 Å.U. on an average size of film. The area completely cleared must have been much less. Possibly a rigid film is blown back less than a liquid one, but the error does

not seem to be large.   The strength of the air blasts has been adjusted so as
to be not much more than that necessary to prevent leakage.

The low compressibility in GH must indicate that the film molecules are
not appreciably displaced relative to one another during compression.   It
has already been calculated, on certain assumptions,* that the cross-section
of a CH_2 group perpendicular to the general direction of the chain is
about 19·3 Å.U.   Probably, then, for all the films in which this portion
of the curves appears, the molecules have their hydrocarbon chains closely
packed in the last stages of compression which precede collapse; and in
many cases the chains are closely packed under quite small compressions.
The figure 21·0 Å.U. is thus obtained as the cross-section of a hydrocarbon
chain as packed in the films, any error being probably so small that the true
value is not greater than 21·2 or less than 20·5 Å.U.

4. *Fatty Acids on Dilute* HCl.

The strength of the solution is of little importance, and the following
remarks apply to N/10 and N/100 HCl solutions equally.   Fig. 2, III, is the
curve obtained with all the fatty acids examined, except the saturated ones
of 12, 13 and 26 carbon atoms, iso-oleic acid ($\Delta\alpha\beta$ oleic acid), oleic, elaidic
and erucic acids.   Brassidic acid, although it has a double bond in the
middle of the chain, does give this curve, and the curves of elaidic and
erucic acids, at temperatures near 0°, are intermediate between this curve
and those to be described in Part III as typical curves of expanded films,
and indicate that, if experiments could be done a few degrees below 0°,
these films would be condensed, and would show the same curve as the
others.   Oleic, lauric and tridecylic acids give expanded curves, and would
not improbably, if condensed films could be obtained, give the same curve.
Cerotic acid behaves much as it did on distilled water, and does not give a
proper film.   Therefore the only real exception to the rule that fatty acids,
saturated and unsaturated, on dilute HCl, give this curve, is iso-oleic acid.
This substance had a very similar compression curve (fig. 2, IV), but the
slope of the lower portion was less steep, cutting the abscissa at a mean
area of 28·7 Å.U., the mean of six experiments on two specimens, both
prepared by Dr. Le Sueur.

There is no hysteresis in these curves, points obtained by removing
weights from the pan and increasing the area lying on the original curve of
compression.   In this respect they are different from fig. 2, II, which records
the behaviour of fatty acids on fresh distilled water, and will be discussed later.

The mean intersection of the lower part with the abscissa is 25·1 Å.U.

* *Loc. cit.*, p. 346.

5. *Esters, Alcohols, Amides, Nitriles and Glycerides.*

Fig. 3, I, gives the compression curve of condensed films of ethyl stearate. Ethyl palmitate and ethyl behenate were identical within the experimental error, and methyl palmitate was very similar. The curve may be taken as a typical curve for a condensed film of an ethyl ester. Below the portion GH there is another nearly straight line cutting the abscissa at 22·3 Å.U. mean value.

Cetyl alcohol (fig. 3) has a similar though less easily seen lower portion,
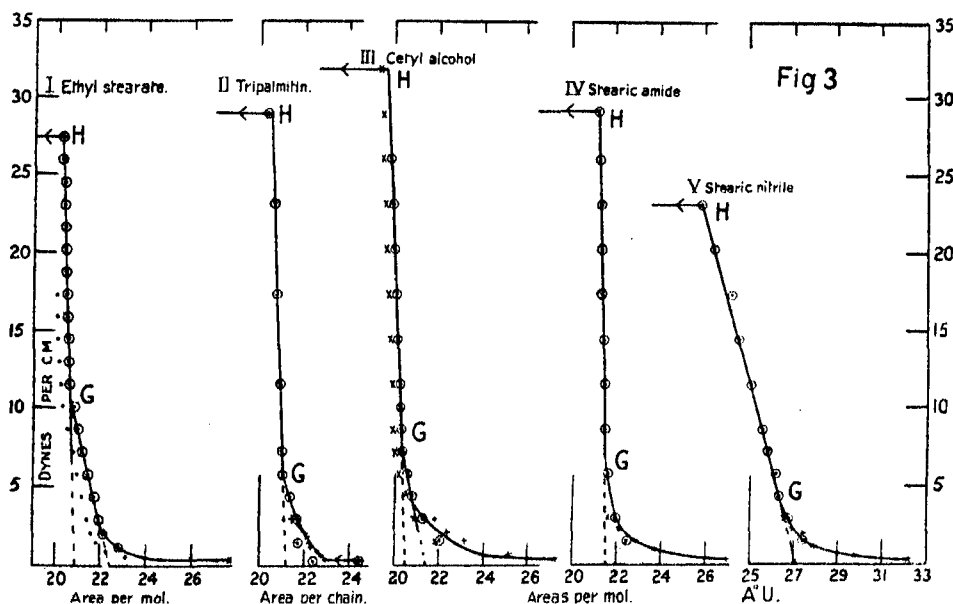
Fig 3

cutting the abscissa at 21·7 Å.U., the mean of eight experiments. This curve is unaltered on HCl.

Tripalmitin (fig. 3, II) shows a slight spontaneous contraction when a low compression is first applied, which is very likely due to the film being very rigid, so that when first put on it is rather in the form of "islands," which do not fit well enough to occupy quite the whole area; and some external compression is necessary to deform these so as to fill the interstitial spaces. Otherwise the curve resembles very closely that of fatty acids on old distilled water. It is doubtful whether there is a distinct lower portion as with cetyl alcohol and the ethyl esters, but, if it exists, its point of intersection with the abscissa is not more than 22 Å.U. The same curve is obtained on HCl. This curve is also given by glycol dipalmitate and tristearin, as would be expected.

Stearic amide (fig. 3, IV) does not show any definite deviation from GH except the tendency to become horizontal, at the lowest compressions, which is common to all the condensed curves, and will be discussed later.

Films of stearic nitrile (fig. 3, V) show an extremely marked lower portion ; indeed (though this may yet prove to be attainable), the line GH has not yet been reached in an experiment on this substance before collapse set in.   The intersection with the abscissa is at 27·5 Å.U.

Esters of alcohols higher than ethyl have also been tested, but since these films even at the lowest temperatures were expanded, they do not afford evidence as to the cross-section of the molecules.   Cetyl palmitate has not yet been tried.

These results are in general agreement with Langmuir's original observations (5).   His curve for ethyl palmitate, taken at 16°, is that of a partially or completely expanded film, and this film is only completely condensed below about 6°.   He stated, however, that tristearin changed on HCl in the same manner as the acids, which is incorrect.   The curves he gave do not agree very well in detail with mine, but his technique was not well suited for avoiding leakage of the film at the barriers.

6. *Cross-section of some Polar Groups.*[*]

The existence of these lower, but quite definite, portions of the curves shows that the films cannot in all cases be regarded as composed of molecules whose *chains* are close packed.   For several reasons, there can be little doubt that the molecules are in direct contact all over the area where this type of curve is found.   In the first place, the form does not in the least resemble that of the curve of an expanded film (Part III); as with other condensed films, variation of temperature over a considerable range has no effect; and, in every case yet studied, when the temperature is raised sufficiently, the films do pass into the expanded condition in the usual way.   It is therefore practically certain that these curves are those of condensed films.

The area is greater than that of the hydrocarbon chains, so that it is clear some part of the molecules have a greater cross-section than the chains.   This part must, moreover, be located in the head of the molecule.   The area per molecule at which the lower line of a curve cuts the abscissa is the maximum cross-section of the head, as packed in the films.   A slight extrapolation is required, but as this portion of the curve is generally nearly straight, it may be made without error.   Whether this is really the area of cross-section of the head group which would be occupied in free space is not certain.

[*] The polar end of the molecule directed towards the water will be called the head, and the hydrocarbon chain, the chain, for brevity.

Table I gives the collected results obtained as to the principal dimensions of various molecules in the films. The lengths of the molecules are not measured directly, but have been deduced from the measurements of area on the possibly dubious assumption that the density in the films is nearly the same as in the acids in bulk. 0·85 has been taken as its value and 21·0 as the area throughout.

$$\text{Length} = \frac{\text{Mol. wt.}}{21 \cdot 0 \times 6 \cdot 06 \times 0 \cdot 85} \times 10^{-7} \text{ cm.}$$

Table I.—Principal Dimensions of Molecules.

Substance.	No. of C's.	Head group.	Cross-sections A.U. (As packed in films).		Approximate length (A.U.).
			Chain.	Head.	
Myristic acid	14	$-CH_2-CH_2-COOH$	21·0	25·1	21·1
Pentadecylic acid	15	$-CH_2-CH_2-COOH$	21·0	25·1	22·4
Stearic acid	18	$-CH_2-CH_2-COOH$	21·0	25·1	26·2
Behenic acid	22	$-CH_2-CH_2-COOH$	21·0	25·1	31·4
Iso-oleic acid	18	$-CH=CH-COOH$	21·0	28·7	26·2
Octadecyl urea	19	$-NH-CO-NH_2$	21·0	26·3	28·8
Stearic amide	18	$-CONH_2$	21·0	not greater than 21·5	26·1
Ethyl palmitate	18	$-COOC_2H_5$	21·0	22·3	26·1
Ethyl behenate	24	$-COOC_2H_5$	21·0	22·3	34·0
Cetyl alcohol	16	$-CH_2OH$	21·0	21·7	22·4
Stearic nitrile	18	$-CH_2CN.$	21·0*	27·5	...

* Not measured directly.

It is remarkable that the presence of the double-bond in iso-oleic acid increases the space required by the head to nearly 15 per cent. more than that occupied by the heads of the other fatty acids.

### 7. *The Mechanism of Rearrangement under Compression.*

In the majority of cases the curves show that simple compression is all that is required to force the molecules in a film from the state in which they are touching at their heads only into the arrangement with close-packed chains. Either the heads themselves must be compressible laterally, with or without a corresponding elongation in the direction of the chain; or, the heads not being sufficiently easily deformed, they must be moved out of the way by a vertical relative movement of adjacent molecules, the wider portions of some finding recesses in the chains of others, so that the total area becomes no greater than that of the cross-sections of the chains.

There is no evidence to enable a choice to be made definitely between these possibilities. It was suggested in the previous paper that the molecules were displaced, and in the next paragraph it will be shown that the head of the

urea derivatives is, below a certain temperature, practically as incompressible laterally as is any other molecule in bulk, but there is no direct evidence as to the deformability or otherwise of the other groups investigated. It is possible that further evidence on the types of film which show one or the other curve may afford the means of making a decision ; and this will lead to some information as to the vertical distribution of molecules in the film, or the depths to which the various molecules are immersed in the water.

8. *The Derivatives of Urea.*

Fig. 4 shows the compression curves obtained on octadecyl urea at two temperatures. They were confirmed on the next lower homologue, heptadecyl urea $(C_{17}H_{35}.NH.CO.NH_2)$. Inset are some determinations of area at an
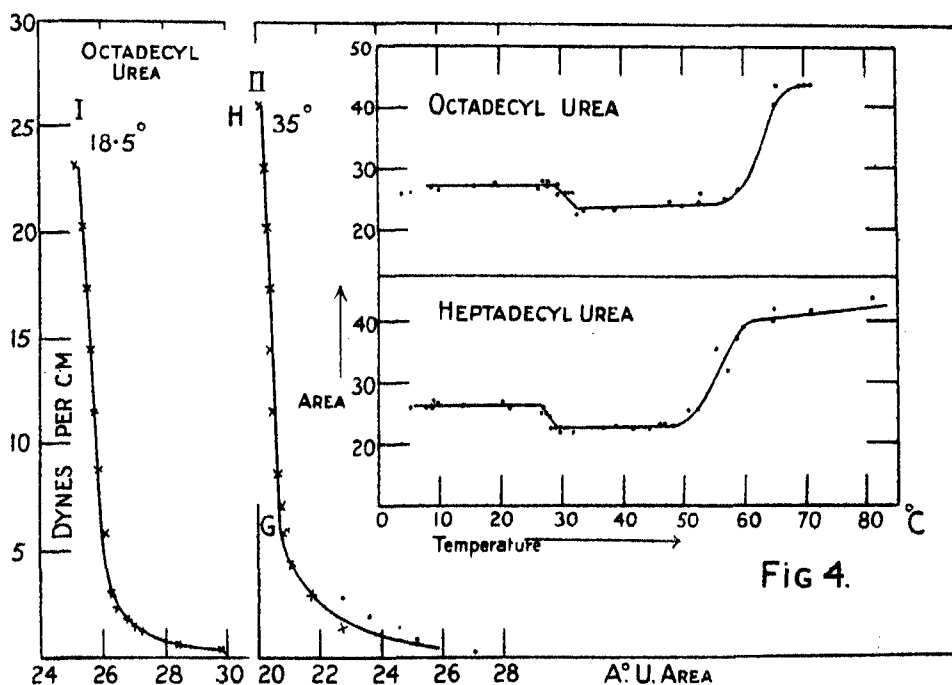
In the inset diagram the areas are at a compression of 1·4 dynes per cm.

arbitrary small compression (1·4 dynes per cm.) plotted against temperature for the two substances. The final rise in these two curves is the ordinary transition to the expanded state common to all substances yet tried ; the fall in area between 29° and 33° for octadecyl urea and between 26° and 29·5° for heptadecyl urea is peculiar to these substances, and is a transition from one condensed film whose compression curve is curve I to another, curve II. The compression curve II shows that very little compression is necessary to pack

the chains closely above the temperature of transition. The curve I shows that no amount of compression will pack the chains closely, however, below the transition temperature. Near the transition temperature there is a short region, not yet fully investigated, where the curves are of an intermediate type, but this range of temperature is of a few degrees only. The curve I gives the cross-section of the heads 26·3 Å.U. (mean value). Probably the reason for the heads offering such resistance to compression or displacement is connected with the fact that these substances have more complicated heads than any of the others investigated; and the powerful orienting and cohesive forces between these heads is also indicated by the solidity of the films below the transition temperature; also the study of the expansion of the films of these substances has given an indication that the cohesive forces are greater than between other molecules of the same length of chain. Whatever is the cause, these two substances are the only ones yet found which show two types of condensed film, with a definite transition temperature between them. Further experiments are intended as soon as possible upon other substances possessing yet more complicated heads.

9. *The Physical State of the Condensed Films.*

As was pointed out in the preceding paper, as well as by Langmuir and others, the films are either solid—that is, circulation tangentially of motes on the surface is stopped—or liquid. The fatty acids, amide, glycerides, and esters all can give solid films when the chains are close packed, though occasionally for some unknown reason, in an individual experiment, the film is not always solid. Some of these films are obviously more rigid than others; the glycerides and glycol dipalmitate are the strongest: and the simple fatty acids and esters the least strong of these solid films, and there is some indication that iso-oleic acid gives stronger films than the saturated acids. A long chain seems to give a more rigid film than a short one. On the other hand, cetyl alcohol films are never solid (as Langmuir first pointed out). Therefore close packing of the chains alone is not a sufficient condition for solidity. The only case yet found of a film being solid in which the heads alone are close packed is that of the ureas. Stearic nitrile and the fatty acids on HCl, below the portion GH, are never solid. Probably the factors which determine the solidity or otherwise depend on small details of the shape of the molecule which may be beyond the power of experiments of this type to detect. No observations have yet been made on the temperatures of transition of the solid into the liquid films; in the previous paper a reference was made to the phenomenon of expansion as "melting," incorrectly, since a more proper term would have been "vaporisation."

10. *The Effect of Age of the Distilled Water.*

A curious effect exists for which no explanation can be given until more experiments have been done, but it must be noticed briefly as if overlooked it is liable to cause confusion in the experiments. Of the substances yet examined, only the fatty acids show the phenomenon; and the solution must be near to a hydrogen ion concentration of $P_H 6$.* If experiments are done soon after the water (or solution) is put in the trough, the film will temporarily resist a compression of 1·4 dynes per centimetre at an area of about 25 Å.U. * There is then fairly rapid contraction to the normal area for close packed chains, completed in about 15 minutes. If weights are put in the pan quickly a curve is obtained like fig. 2, II, the film contracting continually until the line GH is reached. Once this line is reached, further compression merely alters the area along this line ; if weights were removed, usually there was little expansion to the right of the line. This, and a perhaps similar phenomenon, which occurs in the transition region of temperature where one type of the urea films is changing into the other, are the only cases yet found in which there is any hysteresis in the monomolecular films.

If, however, the water or solution is allowed to remain in the brass trough for about 5 days before an experiment, fig. 2, I, is obtained, showing that the chains pack themselves closely almost immediately. What is the change which takes place in the water to alter the films in this manner has not been discovered. It is not the solution of small amounts of fatty acids in the water, for it makes little difference whether experiments have been done on the water during the 5 days "seasoning" or whether the trough has been undisturbed with a cover over it. It is not a change in the hydrogen ion concentration, as it has been noticed on solutions containing phosphate buffers in which the P_H remained constant within 0·1. CO_2 free water, and water nearly saturated with CO_2 at atmospheric pressure, behave like fresh water at first. It makes no difference whether the water has been condensed in silver, tin, or copper, during distillation. Glass distilled water has not yet been investigated for this effect. That the action is on the carboxyl groups is rendered probable by the fact that only the acids show the change.

[*Note added, June* 18.—Water condensed and preserved in glass and used in a glass trough, without any contact with metal, behaved in the same way as the waters mentioned above.]

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* A P_H of 6 denotes a hydrogen ion concentration of 10^{-6} normal.

11. *Solubility of the Films.*

A good deal of qualitative information has been accumulated on the rate of solution of the various substances in the water. The number of molecules passing into solution may be determined without difficulty by observations of any steady decrease in area which occurs under conditions where leaks or measurable spontaneous accumulation of contamination or collapse are absent; and there is usually no difficulty in allowing for small amounts of contamination, if present, by a blank experiment. Solution cannot of course be distinguished from volatilisation directly, but since the rate of disappearance of the substances studied always increased with conditions favouring a stronger attraction between the film and the water, it is improbable that volatilisation was the cause of the contraction.

Solubility depends on a balance in the molecule between the number of polar groups having a strong attraction for the water, and the length of the hydrocarbon chains. The former increase, the latter decrease solution. Higher temperatures accelerate solution.

Upon dilute (N/100) HCl, the rate of solution of all the fatty acids down to lauric is inappreciable at room temperature. On nearly neutral solutions solubility of the acids up to pentadecylic may be noticeable. Addition of one carbon atom to the chain very much decreases solubility. When the C_{15} acid is insoluble, and the C_{14} film decreases at about 1 per cent. per minute, a film of tridecylic acid will disappear about ten times as fast, and the C_{12} acid so fast that before any measurement of area can be taken probably about one-third of the film will have disappeared. Near neutrality, the seasoning effect just mentioned decreases solubility; allowing the solution to stand undisturbed 3 days rendered the solubility of the C_{14} acid inappreciable, while on a fresh solution of the same composition, the C_{15} acid film dissolved at a measurable rate. It was rather surprising to find that for acids above C_{16}, it was possible to obtain approximate measurements of area on N/10 soda, solution taking place only slowly.

12. *Spontaneous Expansion of the Films.*

In two instances the films expanded slowly in area. These were octa-decylamine hydrochloride, on distilled water, and cetyl alcohol on a phosphate solution. Cetyl alcohol films did not expand on distilled water. The rate of expansion, at room temperature, was initially about 8 per cent. per minute for the amine hydrochloride, and 0·2 per cent. per minute for the alcohol. The former rate fell off rapidly with the time, and the latter was not much changed after ¼ an hour.

Such phenomena must be due to a slow combination of the end group of

the film molecule with some constituent of the underlying solution, resulting in an increase of cross-section ; and it is possible that measurements of the rate of expansion may give useful information concerning the progress of some chemical reactions, when the structure of the films is better understood. It is an interesting confirmation of the view that in the condensed films the molecules are closely packed, while in the expanded they are not, that this expansion of the amine hydrochloride film continues up to the temperature at which the expansion becomes nearly complete, but ceases at higher temperatures. The increase in cross-section of the heads of individual molecules may occur, but it is not shown in an increase of the area of the film, unless the molecules are in contact.

13. *Collapse of the Films under Higher Compressions.*

No important difference from the behaviour of palmitic acid films previously described (Part I, p. 348) has been found with any of the substances here investigated. The force required to start collapse is variable. The observation of Labrouste, that when the aggregates ejected from a film are solid they do not spread again into a monomolecular film on removing the compression, has been confirmed. This does occur if the aggregates are liquid.

14. *Form of the Curves at very Low Compressions.*

It was left doubtful in Part I whether or not there was a real deviation from the general linear direction of the curves at the lowest compressions. The lowest forces there measured were 1·4 dynes per centimetre. Later measurements made down to one-fifth of this amount, and, shown in the diagrams, have proved fairly consistent, and show, in all cases, a tendency of the curves to become horizontal at no compression.

If the theory that the expansion of the films, to be described in Part III, is due to the escape of molecules from the condensed or close-packed films is correct, some kind of "vapour pressure" should be expected in the surface, with condensed films below the temperature of expansion. It is possible that this is the cause of the approach to the horizontal in the region now considered. In none of the curves does there appear, however, a horizontal or nearly horizontal, line of any length at a distance from the abscissa greater than 0·4 dynes per centimetre, until the temperature has risen into the transition region between condensed and expanded films (see the next paper), that is, within some 20° of the temperature at which the films are practically completely expanded. The force of 0·4 dyne per centimetre is, on a film of thickness equal to the length of molecules of stearic acid, about 1·5 atmospheres pressure. Thus the pressure exerted by molecules escaping from the

condensed parts of the film increases very sharply as the temperature approaches that of complete expansion.

A fairly sharp intersection of a horizontal line representing the vapour pressure, with the direction of the curve of the condensed film, would be expected on this hypothesis; actually, however, there is no sharp angle but an easily curved line. Possibly the rounding off is due to residual contamination, though in some cases the effect seems rather large to be accounted for in this way; or, there may be some other form of condensed film in which the molecules are in contact in some arrangement very easily disturbed by slight external compression—the arrangement requiring, perhaps, greater cross-sections than those given in Table I. The experiments are not, however, accurate enough to provide real evidence of the existence of any new condensed state.

15. *Experimental Details.*

To the description of the method of experiment given in the preceding paper, some details should now be added. The simplest way of drying the trough after cleaning is to rinse it with boiling water; then it is immediately placed on the levelling screws, the top of the sides wiped dry, if necessary, with clean filter paper, and a solution of paraffin wax in benzene put on with a glass rod, while the trough is warm. The barriers and float are paraffined with the same solution and dried in an oven before use. The use of paraffin wax is absolutely essential to prevent leakage past the barriers, and the top of the sides of the trough must be accurately flat, in order that the glass barriers may touch over the whole width.

Leakage past the floating barrier has been watched for, and the position of the air jets at A and B (fig. 1) adjusted till all leak was stopped. Leaks are one of the most frequent sources of error, and constant vigilance is necessary. Rack and pinion and screw adjustments, giving up and down, side to side, and forward and backward motion, have very much diminished number of failures and the labour of attending to an experiment. It is necessary also to adjust the strength and direction of the air blast so that the balance maintains a constant zero. This can be done with a little experience, without diminishing the strength so much as to allow leaks to occur under high compression.

No correction has been applied for residual contamination. Its total amount has been always small, and it is thought that none of the areas here recorded at temperatures below 35° C. are so much as 2 per cent. too great, from this source of error, where the compression has been greater than about 3 dynes per centimetre. At the lowest compressions measured, this error probably does not exceed 8 per cent. From 35° to 55° C. contamination has

been slightly more troublesome, but probably doubling these limits is sufficient. Above 55°, when the paraffin coating on the sides is melted, it is very difficult to obtain more than three reliable points before the contamination becomes serious; however, by working rapidly, these points may be determined with little more error than below 55°.

Points over the whole range of compressions have generally not been determined in a single experiment. Such a procedure would tend to give too high areas in the later part of the experiment, because a good deal of time must be spent in determining the areas below 3 dynes per centimetre, and at the low compressions the rate of contamination is appreciable. The usual plan has been to determine about five points between 0·35 and 2·8 dynes in one experiment, and in another to commence at 1·4 dynes and add successive increments of 1·4 dynes or 2·8 until the film collapses.

A useful check on the value of a single experiment is afforded by removing weights from the pan. If there has been any leakage or solution of the film there is apparent hysteresis, and an idea can be obtained of the amount of error by comparing the curves of contraction with those of expansion. Any accumulation of contamination acts in the opposite direction to the last two sources of error. Except for the two cases of rather special character mentioned in Section 10, p. 466, I have not yet found a case of real hysteresis among monomolecular films.

The temperature of the trough was regulated by two or three small burners below. There was no difficulty in keeping it constant and uniform to 1° below 35°, to 2° up to 60°, and to 3° up to about 70°. The temperature was read by a thermometer placed in the trough, and it was verified that this indicated the temperature of the surface, by determining the melting point of floating particles of palmitic acid.

Where the substances were not sufficiently soluble in benzene, a small amount of alcohol was added.

The bar F in the diagram was employed for steadying the dropping pipette E, used for measuring the quantity of substance put on. With care, the error in knowing the amount put on should not exceed 3 per cent. in one experiment. The number of molecules in a gramme molecule has been taken as $6·06 \times 10^{23}$.

16. *Preparation and Purification of Materials.*

The saturated fatty acids employed all melted within half a degree of the accepted melting point of the pure substances. Titration in alcoholic solution showed the molecular weights of all those with an even number of carbon atoms to be correct within 1 part in 200, except stearic acid, which as finally

purified had a molecular weight about 0·8 per cent. too low. The acids of an odd number of carbon atoms and the Δαβ-oleic acid were prepared by Dr. Le Sueur, and were undoubtedly of the highest purity when prepared. Verification of the melting points disclosed no sign of deterioration. Oleic acid was an exceptionally pure specimen, prepared in Prof. Lapworth's laboratory. Elaidic, erucic, and brassidic acids had the correct molecular weights. The iodine values were correct for elaidic acid, and indicated about 5 per cent. of admixed saturated acids, probably behenic, for the erucic and brassidic acids. The melting points were those given by Lewkowitsch (6) except brassidic (61°–62° instead of 65°).

Cetyl alcohol was purified till it melted at 50°. Stearic amide and nitrile were prepared from pure stearic acid and purified till they melted constantly at 109° and 42° respectively.

Octadecylamine hydrochloride was prepared by reducing stearic nitrile with sodium and alcohol (7). It was precipitated twice from alcohol by ether; m.p. indefinite, but above 160°. Octadecyl urea was prepared from the preceding by treatment with the theoretical quantity of potassium cyanate; m.p., constant, 111°. Nitrogen, found by the Kjeldahl method, 8·85 per cent.; theoretical, 8·98 per cent.

Heptadecylamine was obtained from stearic amide by the modification of the Hoffmann reaction described by Jeffreys (8); m.p. 54°–56° after redistillation from sodium and boiling to remove CO_2 and water. Heptadecyl urea from the preceding melted constant at 108–9°, agreeing with Jeffreys' determination.

The esters of palmitic acid were prepared by warming together the purified alcohol and palmityl chloride and recrystallising the product from dilute alcohol. M.p.'s: methyl palmitate 29·5°–30°, ethyl 25·5°, *n*-propyl 15°–16° *n*-butyl 13°–14°, iso-butyl 19°–23°, iso-amyl 11°–12°, *n*-octyl 24°–25°. Other esters were prepared in the usual way. A few specimens were found by titration to contain small amounts of free acid (as palmitic), up to 2 per cent.

Tripalmitin and tristearin were purified to have the correct saponification values within 0·6 per cent.; m.p.'s: 63–4° and 68·5°–69·5°.

Glycol dipalmitate had the m.p. 70°; this appears to have been incorrectly recorded in the original paper as 65° by a clerical error (9). The specimen was the original one prepared by Miss Stephenson.

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The Corrosion of Iron and Steel.

By Sir ROBERT HADFIELD, Bt., F.R.S.

Introduction.

The subject of the corrosion of iron and steel is a most important one, yet with the exception of a minor contribution by Dr. E. Newbery and the author in 1916, no communication has been presented to the Royal Society for the last one hundred years. This paper refers to the wastage of the world's iron and steel due to corrosion, and describes a number of recent experiments carried out by the author with regard to copper-steel. It is hoped that these results will add to the general knowledge on this subject of corrosion from both the scientific and practical point of view.

Careful estimates appear to show that there is a present annual loss of over 40 million tons of iron and steel under corrosion and consequent removal of material rendered unserviceable. Taking into account the cost of protecting the material, the author estimates that the aggregate annual loss due to the effects of corrosion is probably well over 500 million pounds sterling, based on prices which have prevailed during the last few years.

The introduction of alloy steels which possess high capacity for resisting corrosion should be encouraged, and although higher in the first cost they will probably be found more economical in the long run.

The great importance of economy in the use of iron, and of studying methods to avoid or reduce rusting or oxidation, is shown by valuable and interesting statements in a recent article, ' Iron Ore in Europe,' by Prof. J. W. Gregory, one of our Fellows. In reviewing a report by Mr. Max Roesler, of the U.S.

Geological Survey, on the iron ore resources of Europe, Prof. Gregory says it appears from this statement that the reserves of iron ore in the world are estimated only to be sufficient to maintain the same rate of production as in 1913 for 1000 years. On the other hand, if the output of iron should increase, as is quite possible, in fact probable, in the same ratio as the pre-war rate of even only 5 per cent. per annum, then the world's supplies will be exhausted in about 150 years. A serious statement indeed!

Last year the total production of pig iron, which is the basis of practically all iron and steel, was only 35 million tons as against the pre-war maximum of 78 million tons, but this reduction can only be a temporary one. For example, supposing the Chinese commenced to use iron and steel on a large scale, the demand on the iron ore supplies of the world would be very great, as the present output of pig iron would soon be doubled. Dr. J. S. Unger, Research Engineer of the Carnegie Steel Company, states that if this country, China, used steel in the same quantity *per capita* as the inhabitants of the United States, half a million tons of steel would be consumed every 24 hours.

It may be interesting to add, as showing the enormous output in the United States—and that their use of the metal iron is not likely to decrease, but will surely increase—each blast furnace there has an average output of 120,000 tons per annum, Germany 55,000 tons, and England 28,000 tons.

In 1913 each person in the United States used 700 lb. of iron, and in 1917 the production *per capita* was nearly half a ton. A similar use in this country would mean that we should have to produce about 23 million tons of pig iron, and even at the American rate of output for 1913, our production would have to be 14 million tons. As a matter of fact, the maximum output in Great Britain has not yet reached 11 million tons.

Whilst Prof. Gregory's estimate is necessarily to some extent speculative, yet such a statement from an authority on the subject shows how great is the importance of studying this question of corrosion more closely than has been done in the past, in order to lead to economies being effected.

Dealing first with the work of the Institution of Civil Engineers, by the kind permission of the Corrosion Committee of the Council of that body, the author is able to explain the research work now in hand and its objects. An interim report on the progress of the research will shortly be published by the Committee, and will show the work completed up to the present time. The work was commenced by the formation, in 1916, of a special Committee, under the able guidance of its Chairman, the late Sir William Matthews, K.C.M.G., to deal with problems with regard to the deterioration of structures

exposed to sea action. Its present Chairman is Mr. Maurice Wilson, M.Inst.C.E. Encouragement in funds has been provided in a generous manner by the Department of Scientific and Industrial Research, who recognise the great value of the investigations. The total grants from this source have amounted to several thousand pounds.

Description of the Ferrous Materials Employed in the Research.

The specimens prepared by the author are represented by 14 types of ferrous material, in all 1,330 specimens, of which 955 have already been allocated by the Committee for the Sea-Water Corrosion Tests, also those required for mechanical, microscopical, and other laboratory tests.

The materials, classified into four main sections, are indicated in Table I, together with a very complete analytical record of their chemical composition.

The wrought iron, Section I, was furnished by the Low Moor Iron Company, and the "Armco" iron by the Shelton Steel and Iron Company. The carbon steels and special steels, Sections II and III, were produced under specification fixed by the author, and were made by Hadfield's, Limited, of Sheffield, while the cast iron, under Section IV, was supplied by the Lilleshall Company.

The specimens in all cases, excepting naturally the cast irons, are prepared from rolled bars 3 inches in breadth by $\frac{1}{2}$ inch in thickness, the length of each specimen being 24 inches. In order to carry out the tests under conditions as nearly as possible resembling those met with in constructive work, the specimens are prepared in the condition "as rolled" without further heat treatment, being allowed to retain the oxide skin produced in rolling (in the case of the cast irons the casting skin). There is, however, a small number of specimens included experimentally from which the skin had been removed by grinding.

In view of the importance of the subject some of our Fellows might like to have test pieces of the author's own specimens, prepared over many years, with which to experiment, that is, ordinary and alloy steels of a large variety of types. If so, the author will willingly place, without cost, sets of these specimens at the disposal of those Fellows interested.

The tests included complete analytical tests, including the percentage determination of carbon, silicon, sulphur, phosphorus, and manganese, and in the special steels, also nickel and chromium ; also mechanical tests, comprising tensile, shock, and hardness tests. In addition, the micro-structure of all the materials has been examined and photographed in view of its important bearing on corrosion.

The total number of individual tests made is 203, made up as follows :—

26 tensile tests, 104 Fremont shock tests, 26 Izod shock tests, 26 micro-test pieces, 21 test pieces for laboratory corrosion tests. 78 Brinell-Ball hardness tests were also made.

The specimens have been despatched to testing stations at Auckland, Colombo, and Halifax (Canada), also to Plymouth. They are made up in various forms, and the points under investigation cover :—The effects of total and intermittent ("half tide") immersion and exposure to marine atmosphere ; also corrosion in fresh water. Variations in corrosion arising from geographical situation. The influence of strain in the metal, and of surface scale arising from the manufacturing operations ; also of certain structural details, that is, items such as bolts and rivets, and the contact of dissimilar metals. The mechanical properties of the corroded materials will also be investigated.

The particulars given will, the author hopes, give a sufficient outline of the scope and bearings of this important research. The work of the Committee in planning the details has required very careful thought, and the preparation and arrangement of such a large number and variety of specimens has been no easy task, great care, in particular, being necessary to avoid the possibility of mixing, which might easily occur in 1500 specimens of so many types of material.

The Resistance to Corrosion of Steel containing Copper.

It has been stated in America that mild steel containing a small percentage of copper has proved superior in resisting corrosion, as compared with ordinary mild steel. Such a ready and inexpensive means of mitigating the evils of corrosion is naturally attractive, specially as mild steel forms the great bulk of the world's structural steel. The author has therefore been led to make a particular study of these claims.

The American tests of the copper steel, which formed part of an extensive research with a variety of materials and conditions of exposure, were carried out by the Committee of the American Society for Testing Materials. The results are published in a Report of the Committee, dated 1920, and in a number of papers* by Mr. D. M. Buck, Metallurgical Engineer to the American Sheet and Tinplate Company, Pittsburg. For the precise

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* 'Research on the Corrosion Resistance of Copper Steel'; 'Recent Progress in Corrosion Research'; 'Copper in Steel—The Influence of Corrosion'; 'Copper in Steel Tie-Plates'; 'Influence of a very Low Percentage of Copper in Retarding Corrosion'; A Review of the Development of Copper Steel.'

Table I.—Description of the Materials used in this Research, and their Analysis.

Type of material	Classification letter	Analysis								Treatment*
		C.	Si.	S.	P.	Mn.	Cr.	Ni.	Cu.	
Section I.—Irons (Rolled and Forged).										
Wrought iron	N.	0·02 / 0·01	0·14 / 0·15	0·013 / 0·012	0·113 / 0·114	Tr. / 0·03	—	No. 1 bar / No. 2 bar		970° water. / 560 "
Swedish charcoal iron	P.	0·02 / 0·04	0·03 / —	0·019 / —	0·022 / —	0·01 / 0·03	—	—	— / —	970 " / 560 "
"Armco" iron	M.	0·03 / 0·04	0·03 / 0·04	0·032 / 0·033	0·016 / 0·019	0·06 / 0·07	—	No. 1 bar / No. 2 bar		970 " / 560 "
Section II.—Carbon Steels.										
Mild steel with low Mn. and high S. and P.	B.	0·21 / 0·22	0·17 / —	0·090 / 0·115	0·060 / 0·073	0·33 / 0·35	— / —	—	—	900° water. / 650 "
Mild steel with 0·7 per cent. Mn.	F.	0·23 / 0·25	0·16 / —	0·061 / 0·064	0·048 / —	0·68 / —	— / —	—	—	900 " / 700 "
Medium carbon steel with low S. and P.	E.	0·34 / 0·35	0·2) / —	0·024 / 0·026	0·027 / —	0·71 / 0·72	— / —	—	—	900 " / 650 "
0·40 per cent. carbon steel	D.	0·40	0·20	0·049	0·045	0·85	—	—	—	900 " / 650 "
Section III.—Special Steels.										
Mild steel plus ½ per cent. copper	G.	0·21 / —	0·14 / —	0·043 / —	0·046 / —	0·94 / 0·95	— / —	— / —	0·63 / 0·64	850° water. / 650 "
Mild steel plus 2 per cent. copper	H.	0·22 / 0·23	0·14 / —	0·033 / 0·035	0·041 / 0·043	0·90 / 0·92	— / —	— / —	2·18 / 2·19	850 " / 700 "
3½ per cent. nickel steel	K.	0·31	0·18	0·029	0·038	0·54	—	3·75	—	850 " oil. / 650 water.
36 per cent. nickel steel	L.	0·09 / 0·15	0·09 / —	— / —	— / —	0·77 / 0·97	— / —	36·43 / 36·67	— / —	940 " / 875 "
Non-rusting steel	J.	0·36	0·22	—	—	0·13	13·57	—	—	750 "

Section IV.—Cast Irons.

Hot blast cast iron	Q.	a1 ·88 b1 ·07 c2 ·95	2 ·16	0 ·105	0 ·856	0 ·28	No. 1 bar	
		a1 ·84 b0 ·94 c2 ·78	2 ·52	0 ·103	0 ·84	0 ·26	No. 2 bar	Not heat treated.
Cold blast cast iron	R.	a2 ·75 b0 ·72 c3 ·47	1 ·66	0 ·067	0 ·455	0 ·74	No. 1 bar	
		a2 ·55 b0 ·80 c3 ·35	1 ·77	0 ·066	0 ·50	0 ·73	No. 2 bar	Not heat treated.

a = graphitic carbon.   *b* = combined carbon.   *c* = total carbon.

* Under this column is given the heat treatment to which one specimen of each material was submitted for the purpose of mechanical test, that is in addition to the test carried out representing its condition as submitted to corrosion. "970° water and 560° water" means, for example, that the specimen was at about 20° C., afterwards heated to a temperature of 560° C., and quenched again.

behaviour of the copper steel, under various conditions of exposure, these papers should be referred to.

Experiments* on copper steels made by Prof. O. Bauer, of Berlin, have shown that under most conditions the influence of copper is uncertain, and only in the sulphurous atmosphere of manufacturing districts has the copper any perceptible restraining influence against corrosion—the latter fact is rather confirmed by laboratory tests. As a general conclusion, it is considered that the addition of copper for the purpose of preventing or mitigating corrosion, would not be generally advisable. Copper is most beneficial in those steels relatively high in phosphorus content, and the results therefore in this respect differ from those of Mr. Buck quoted above, in which the *rôle* of copper is believed to be that of neutralising the harmful effects of sulphur.

The amount of copper in the specimens investigated ranged from 0·1 to 0·4 per cent., and in the author's opinion the value of the research would have been enhanced had some specimens free from copper been included for comparison.

In a preliminary examination of the question the author made the following tests. Two clean and polished specimens, one (No. 2824) of mild steel containing 0·16 per cent. of copper, and another (No. 2825) of wrought iron, were completely immersed in artificial sea water for 48 hours at 80° F., with results as follows. (The loss of weight, following the usual practice in the Hadfield Research Laboratory, was determined after removing loose corrosion products by rubbing the specimens with hard soap. Such treatment it has been found does not remove any appreciable amount of uncorroded steel.)

Specimen No.	Material.	Analysis.						Size of specimens.	Loss in mgrm. per sq. cm. exposed to corroding action.
		C.	Si.	S.	P.	Mn.	Cu.		
		p.c.	p.c.	p.c.	p.c.	p.c.	p.c.	cm.	
2824	Steel containing Cu	0·20	0·01	0·078	0·043	0·50	0·16	12·5 × 2·5 × 0·25	4·2
2825	Wrought iron	0·11	0·01	0·073	0·345	0·47	0·02	12·5 × 2·5 × 0·25	3·2

Under these conditions, therefore, the results show that steel containing 0·16 per cent. of copper is less resistant than wrought iron.

Later the author was kindly favoured by Mr. D. M. Buck with specimens of the American copper steels, in the form of pieces from rolled sheets suitable for corrosion experiments, together with similar specimens from the same heat

* 'Stahl und Eisen,' vol. 34, pp. 37–45, January 13, 1921; also pp. 76–83, January 20, 1921.

of open-hearth steel to which copper had not been added. Mr. Buck's analyses of the two materials are as follows :—

	C.	Si.	S.	P.	Mn.	Cu.
5127 A......	0·12	0·008	0·037	0·023	0·53	0·268
5127 B......	0·14	0·007	0·038	0·023	0·53	0·018

With these specimens a number of corrosion tests have been carried out by the author under the varying conditions indicated in Table II. In every case the specimens were tested in pairs, that is one specimen of the steel (A) containing copper and another of the steel (B) free from copper exposed simultaneously. All conditions as regards manipulation and exposure were identical for the two materials.

The specimens were received from Mr. Buck covered with their oxide scale produced by the rolling process, and as this represents the condition under which such material would in general be used, the exposure tests in the atmosphere and in artificial sea-water were carried out with this skin intact. Duplicate specimens were, however, prepared and exposed simultaneously, from which the skin had been removed, the surface then being polished until free from visible scratches.

Atmospheric corrosion was observed both in the pure country air at Hathersage, 11 miles from Sheffield, and also simultaneously in the rather sulphurous atmosphere of the manufacturing district of Attercliffe, Sheffield, where the Hecla Works are situated. This exposure took place, as it happened, during the exceptionally dry period of the summer of 1921.

The remaining tests have been carried out under laboratory conditions. In these the specimens were immersed for a period of 21 days, cleaned and weighed and the loss recorded. In this condition without further preparation they were re-immersed for a period of three months.

For the short-period tests—7 days—shown in Table II, specimens were used which had already been tested in other ways. The effects of the previous test, however, had in these cases been obliterated by removing the surface to a sufficient depth and repolishing.

From these results the author draws the following conclusions as regards the behaviour of the two materials under the various types of corrosion.

(a) *Atmospheric Corrosion.*—The copper steel is rather less corroded than the ordinary steel, but especially so in the more corrosive industrial atmosphere at Attercliffe. This applies to both material with rolling scale on and with the same removed. Material with the scale removed is more resistant than with the scale on, confirming what is generally found to be the case.

(b) *Sea-Water.*—The ordinary steel corrodes the more rapidly at first;

Table II.—Comparative Corrosion Tests of Mild Steel with and without
Addition of Copper.

Specimens 0·06″ × 6″ × 3″ supplied by Mr. D. M. Buck.   Area 240 sq. cm.

Analysis.	C.	Si.	S.	P.	Mn.	Cu.
A1—8	0·12	0·008	0·037	0·023	0·53	0·268
B1—8	0·14	0·007	0·038	0·023	0·53	0·018

Specimen No.		First exposure.			Second exposure.		
		Period.	Loss in mgrms. per sq. cm.	Relative loss. Mild steel = 100.	Period.	Total loss in both periods. Mgrms. per sq. cm. of original surface.	Relative loss. Mild steel = 100.
Atmospheric at Hathersage.							
A 1	R.	3 months	7·1	90			
B 1	R.	3 „	7·87	100			
A 1	S.	3 „	9·13	75			
B 1	S.	3 „	12·10	100			
Atmospheric at Attercliffe.							
A 2	R.	3 months	18·40	75			
B 2	R.	3 „	24·70	100			
A 4	S.	3 „	22·40	77			
B 4	S.	3 „	29·00	100			
Artificial Sea Water. A 3·1 per cent. solution of Tidman's Sea Salt in Sheffield Tap Water.							
A 3	R.	21 days	1·33	69	3 months	6·38	91
B 3	R.	21 „	1·93	100	3 „	7·00	100
A 6	S.	21 „	1·43	64	3 „	7·57	97
B 6	S.	21 „	2·22	100	3 „	7·77	100
Coal Tap Water (Sheffield).							
A 7	S.	21 days	1·33	72	3 months	9·30	101
B 7	S.	21 „	1·85	100	3 „	9·16	100
50 per cent. Sulphuric Acid in Sheffield Tap Water.							
*A 3	R.	7 days	1·73				
A 8	S.	21 „	32·90	70	3 months	41·42	18
B 8	S.	21 „	46·80	100	3 „	315·80	100
20 per cent. Sulphuric Acid in Sheffield Tap Water.							
*A 8	R.	7 days	24·3	8			
*B 3	R.	7 „	309·0	100			

For the second exposure period the specimen was in the condition as left after the loose corrosion products from the first test had been removed for weighing.

R. indicates rolling scale removed initially and surface polished.

S. indicates rolling scale on the specimen.

* Indicates specimen had been used for an earlier test, corroded surface removed then repolished.

The volume of corroding medium in the laboratory tests was 1 litre.

In the case of the exposures for 3 months in artificial sea water and tap water, the liquid was changed every 14 days, the loose rust being washed off in running water before re-immersion.

In the case of the exposures for 3 months in 50 per cent. sulphuric acid, the liquid remained unchanged throughout the period.

subsequently the rate of corrosion for both materials slows up, indicating a certain degree of "self-protective" action, which is rather more pronounced for the ordinary steel. This is best seen in fig. 1. At the end of 16 weeks,
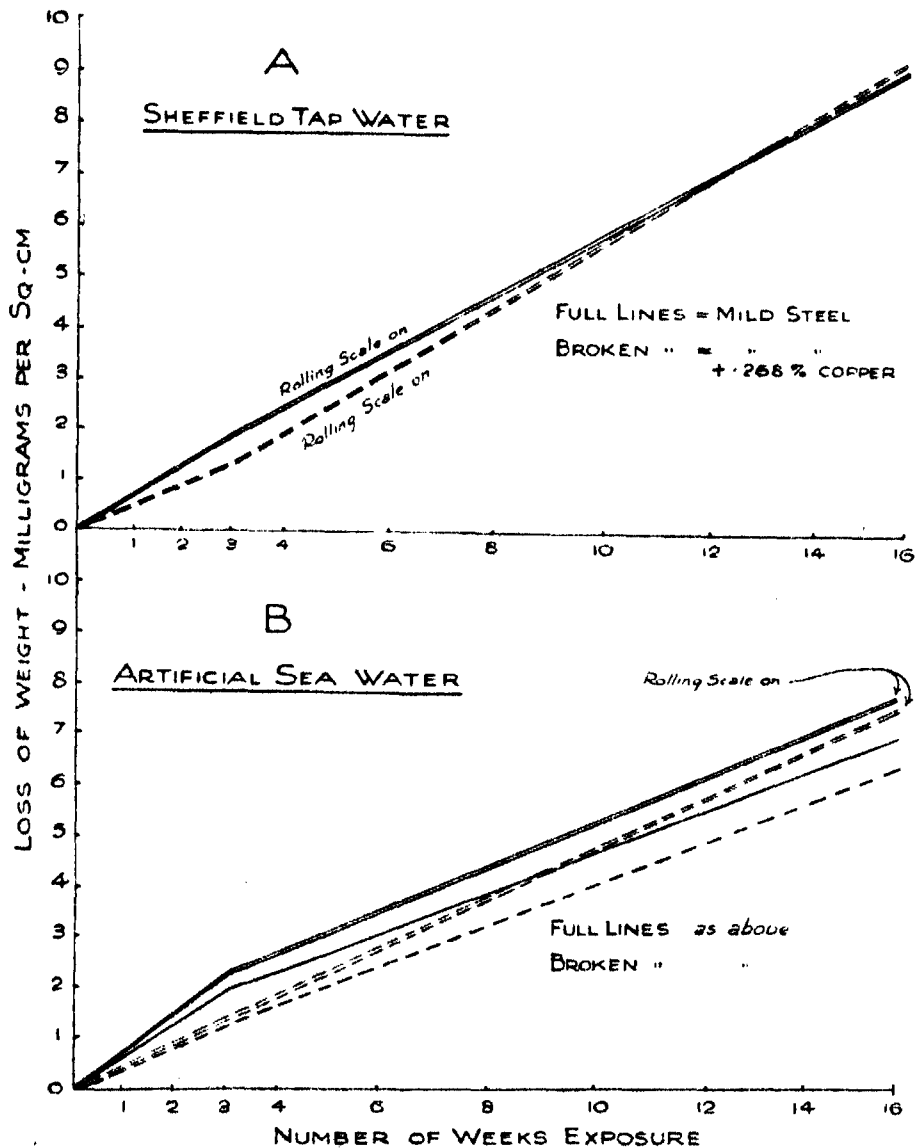
FIG. 1.—Tap and Sea Water.

however, the total extent of the corrosion of the copper steel is still less than that of the ordinary steel. The relative behaviour of the material with scale on and that with the scale removed is the same as for atmospheric corrosion.

(c) *Tap Water.*—There is little to choose between the two materials, which maintain a fairly constant rate of corrosion over nearly 4 months. The tap water, which initially is not so corrosive as sea-water, over the longer period is more corrosive, due to the absence of self-protective action of the steels against this medium. In this case no specimens were tested with their rolling scale on.

(d) 50 *per cent. Sulphuric Acid.*—With the original scale on, both materials were attacked very rapidly at first; while, however, the rate is maintained subsequently for the ordinary steel, that is solution goes on at a steady rate, when re-immersed after a 3 weeks' exposure and weighing, the steel containing copper is only very slowly attacked. During the 3 months' period of the second immersion the rate of corrosion is only about one-sixteenth of the rate during the first period of 3 weeks. Apparently, therefore, when the scale has become detached and the attack takes place more directly on the surface of the steel, the steel containing copper is very resistant to a 50 per cent. solution of sulphuric acid. That this is so was confirmed by a 7 days' test on a freshly prepared and polished specimen free from scale (see fig. 2).

(e) 20 *per cent. Sulphuric Acid.*—A seven days' test on specimens with the scale removed, while showing more vigorous action than the 50 per cent. solution, confirms the great superiority of the steel containing copper against attack by sulphuric acid (see fig. 2).

In the author's tests, therefore, the conclusions arrived at, both from the American and the German tests, as to the superior resistance of mild steel containing a small percentage of copper to atmospheric corrosion, are borne out, not however to the extent shown by the American tests. The superiority amounts to about 10 per cent. in pure air, increasing to about 25 per cent. in an industrial atmosphere.

As in the German tests, the results of immersion in sulphuric acid point strongly to this superiority under atmospheric corrosion being due to and dependent on the amount of sulphurous impurity carried by the air.

The author's tests, so far as immersion in ordinary water is concerned, confirm Dr. Cushman's opinions, and also the German conclusions, that is, no advantage for the copper steel is to be looked for in this direction. In sea water the above tests indicate, at any rate for a comparatively short period of exposure (a few months), a certain superiority for the copper steel. With a very long period of exposure, however, it is possible this superiority may be wiped out, or even negatived, and in this respect again they bear out Dr. Cushman and the German conclusions.

It has been suggested that the very outstanding results obtained in America for the copper steels were to some extent due to the superior

physical condition of the steel as compared with the ordinary mild steel.
A pair of tested specimens received from Mr. Buck through Dr. Friend
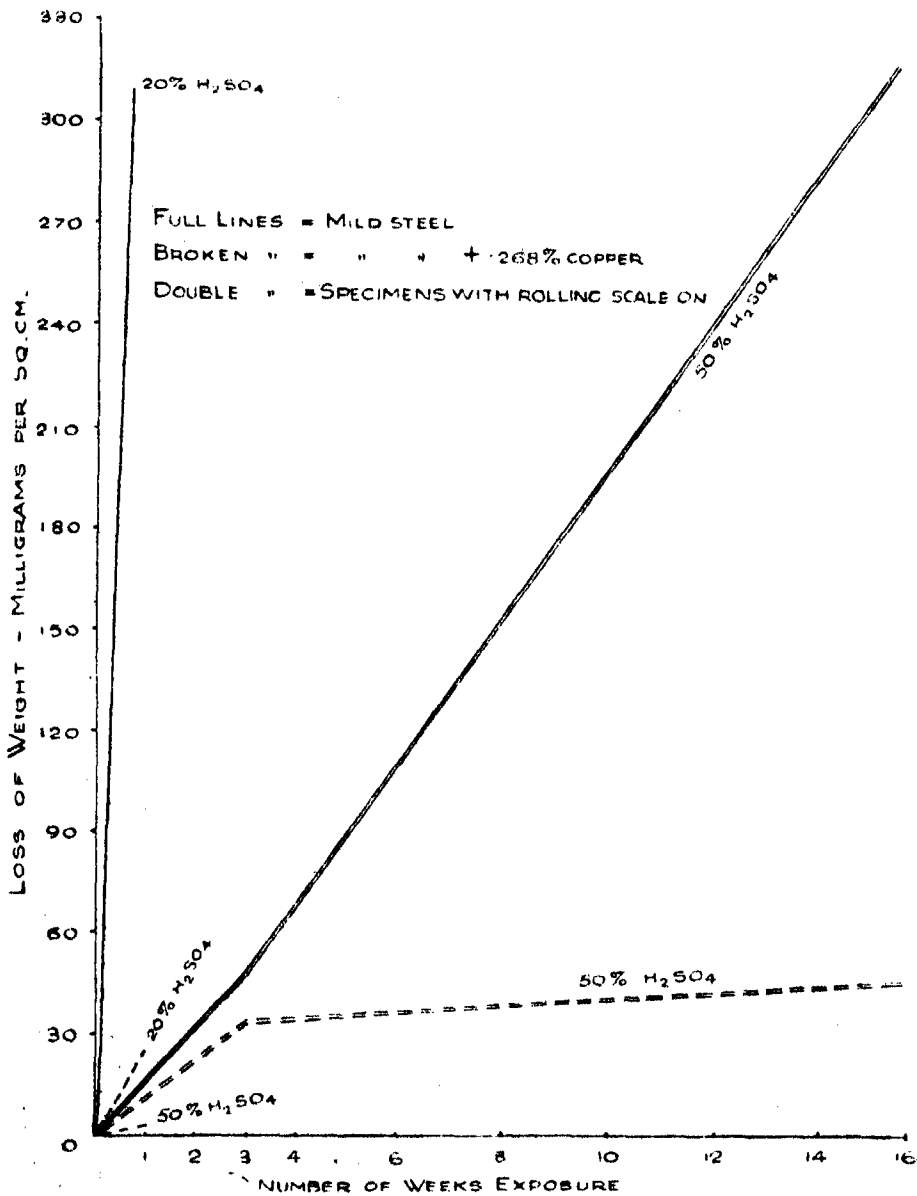
FIG. 2.—Sulphuric Acid.

gives some support to this idea. These specimens, of corrugated sheeting,
have been exposed for twenty-three months to the atmosphere at Atlantic

City, U.S.A.; the copper steel was very little corroded, while the ordinary steel had become very thin, with a number of holes corroded completely through the sheet, the surface otherwise badly pitted. The latter, on examination, showed a particle of scale at the bottom of each pit, forming a centre for corrosion, and it was evident that in rolling the material had been very much oxidised and the scale rolled deeply into the sheets. The scale from the copper steel sheet had been completely corroded off in an even manner, and left no pockets containing scale, a circumstance of undoubtedly favourable influence in determining the subsequent behaviour of the sheet.

The specimens on which the above series of tests were carried out by the author do not show any marked difference in the nature or amount of the scale as between the two materials. Micrographic examination, however, showed a difference in structure between the materials, that is, as received and as tested above. While both materials showed the usual character of mild steel, that is, mainly ferrite grains with carbon distributed in the form of carbide of iron; in the case of the steel containing copper, the carbide is invariably confined to the grain junctions; in the mild steel, on the other hand, the carbide is indiscriminately distributed throughout the material. In these circumstances it was not possible to attribute the superior qualities of the copper steel definitely to the presence of copper *per se*, since it is known that physical condition in general has a distinct influence on corrosion.

In order to investigate this point further, therefore, the author carried out the following tests :—

Pieces cut from specimens A1 and B1 (previously tested under atmospheric corrosion) were heated together to 800° C. and cooled in air. This had the effect of normalising both materials, and their micro-structures were then identical, the carbide, in the form of pearlite, being evenly distributed.

After the surface had been removed to a sufficient depth to take away the scale produced by heat treatment and the effects of the previous corrosion tests, and the specimens polished, they were submitted to a further test for twenty-one days in 50 per cent. sulphuric acid, as shown in Table III.

The result shows that even under these more comparable conditions the copper steel is by far the more resistant against attack by sulphuric acid. The relative rates of corrosion are as nine to one. Further specimens tested on the same lines, but heat-treated at 900° C. instead of 800° C., gave full confirmation. The author's experiments, therefore, show that even so small an amount of copper in mild steel as 0·25 per cent., or only 1 part in 400, can exert a very marked inhibiting influence against corrosion by sulphuric acid, and against atmospheric corrosion, in so far as the latter is due to

sulphurous impurities in the air. What precisely is the manner in which the copper effects this improvement is at present little understood and difficult to investigate. Further work is, however, being undertaken in order to obtain information if possible on this point.

Table III.—Corrosion Tests on Specimens of Mild Steel, with and without Additions of Copper, in Similar Physical Condition.

The materials are the same as those referred to in Table II.

Specimens immersed in 50 per cent. sulphuric acid, by volume, for 21 days.

Size of specimens 0·15 × 7·6 × 2·5 cm. Area 40 sq. cm.

Analysis.	C.	Si.	S.	P.	Mn.	Cu.
A1	0·12	0·008	0·037	0·023	0·53	0·268
B1	0·14	0·007	0·038	0·023	0·53	0·018

Rolling scale removed and specimens polished.

Specimen No.	Heat treatment.	Loss in mgrms. per sq. cm.	Relative loss. Mild steel = 100.
A1	Heated to 800° C. and cooled in air	4·8	11
B1	Heated to 800° C. and cooled in air	43·8	100
A1	Heated to 900° C. and cooled in air	4·2	8·4
B1	Heated to 900° C. and cooled in air	50·2	100

Conclusion.

It seems wise to include a few words of caution in regard to forming general conclusions as to whether a small percentage of copper as a constituent of steel is really desirable for general service conditions. As shown in this paper, a small copper-content, say 0·16 to 0·25 per cent., is beneficial, provided the condition is that of *bare* metal exposed to atmospheric corrosion, especially in a sulphurous atmosphere. But no recorded tests have yet shown that *coated* metal would be benefited by a copper-content. Some investigators have held that, so far as galvanised metal is concerned, the purer the base metal or the freer it is from impurities the longer life will be obtained in average service.

Unquestionably, in the majority of service conditions, iron or steel is subjected to either total or partial immersion in natural waters, or some sort of liquid phase. It is by no means certain yet that, under such conditions, a copper-content in steel might not actually be deleterious, and it is fair to state that this opinion is held very strongly by Dr. Cushman and other investigators who have been long studying these problems. The study is exceedingly difficult, owing to the fact that a given type of iron or steel, which may

behave very well under one set of conditions, will quite reverse its behaviour under another set. It is necessary, therefore, to proceed with extreme care before drawing important conclusions on the basis of any tests so far carried out, which might be the means of inducing steel manufacturers generally to introduce copper as a commercial constituent of mild steels.

It should be noted that if such a practice came into general use, the scrap of the steel manufacturing countries would become greatly infected with copper, which is not thereafter removable by the various refining processes now employed. If future experience should tend to show that a copper-content was in many cases deleterious rather than beneficial, this would be a most serious and important consideration.

In this paper the author has not considered the question of the high chromium-steel alloys containing about 12 per cent. of chromium and from 0·10 to 0·60 per cent. of carbon, known under the names of "rustless," "stainless," and "non-corrosive." Such material is very expensive, and does not immediately concern the ordinary user of iron and steel in large quantities. If these experiments help to show how it is possible to obtain steel as little subject to corrosion and lower in cost than the type just mentioned, they will have served a useful purpose, as well as drawing the attention of our Society to this important subject.

In these various researches, carried out at Hecla Works, Sheffield, the author has had the assistance freely rendered of Mr. I. B. Milne, B.Met., and Mr. W. J. Dawson; also Mr. T. G. Elliot, F.I.C., as regards analytical and micro-examination and the corrosion tests; Mr. S. A. Main, F.Inst.P., has given general supervision and arranged the specimens. The author takes this opportunity of expressing his best thanks to those who have rendered valuable assistance in this research.

Boundary Lubrication.—The Temperature Coefficient.

By W. B. HARDY, Sec.R.S., and IDA DOUBLEDAY.

(Received June 20, 1922.)

The experimental method employed was that described in earlier papers.[*] A slider having a spherical face is made to slide over a plate in an atmosphere of rigorously clean and dry air. The friction measured is static friction and the object of the experiments the determination of the effect of temperature. This has now been studied over a range of 15° C. to 110° C., and it may be said at once that the relations discovered are of a totally unexpected character.

More than one attempt to study the effect of temperature was defeated by the fact that lubricating vapours were given off from the walls of the chamber in which the plate and slider were enclosed. This difficulty was completely removed by using a chamber with double walls, the inner wall being a continuous sheet of nickel. Between the walls were placed the electric grids for heating the chamber. The stream of dry air with which the chamber was flooded was also heated by being passed through a tube of silica, which was maintained at the required temperature by a coil of wire through which a current was passing. The temperature of the stream of air and the temperature of the chamber were recorded electrically.

Temperature might influence friction by altering the state of the solid faces or of the lubricant; it was, therefore, necessary to study clean faces first.

Clean Faces.

Glass was found to be totally unsuitable for use because the physical state of its surface was profoundly altered by a relatively small rise of temperature. The figures in Table I illustrate this.

Table I.—Glass.

Time elapsed.	Temperature (° C.).	Pull.	μ.
5 minutes	15·5	25·5 grm.	0·94
80 ,,	15·5	25·5 ,,	0·94
70 ,,	73	13·6 ,,	0·51
100 ,,	74	12·1 ,,	0·46
130 ,,	74	12·1 ,,	0·46
180 ,,	15·5	12·0 ,,	0·46
240 ,,	15·5	12·0 ,,	0·46

[*] 'Proceedings,' A, vol. 100, p. 550.

It will be noticed that the coefficient of friction (μ = pull ÷ weight of slider) falls as the temperature rises, and that the changed state of the surface which this indicates is not reversed when the temperature falls.

The fall in friction was greater the higher the temperature to which the glass was exposed. Thus glass at 74° reached a steady state in about 30 minutes with μ = 0·46, but at 110° in 45 minutes with μ = 0·36. The effect is due to the formation of a film which prevents water from wetting the surface, and which cannot be removed by soap and water; it is, however, destroyed by hot chromic acid and the friction then returns to the full " clean " value characteristic of the particular sample of glass.

Quartz, when cleaned in the way ordinarily used for glass, namely, by heating in a strong solution of chromic acid and rinsing in tap water, behaved like glass as the values given in Table II show :—

Table II.—Quartz.

Time.	Temperature (°C.).	μ.
0 minutes	17	0 ·73
30 ,,	17	0 ·75
65 ,,	72	0 ·13
		(slow glide)
120 ,,	110	0 ·09
175 ,,	20 ·5	0 ·08

By this time we were aware of the fact that the friction of steel and bismuth is not affected by temperature. This suggested that the behaviour of quartz might be due to a film obstinately adhering to the surface, and not to the substance itself. The suggestion proved to be correct, since the fall in friction observed with rise of temperature did not appear when the quartz faces were vigorously rubbed with the fingers under a stream of water, after having been heated in the chromic acid bath. It is not unlikely that this film on quartz, which resists hot chromic acid and needs actual traction for its removal, is itself a glass due to surface reaction of the silica with alkali from the air or from polishing or cleansing substances.

The values in Table III are for fully cleaned quartz. It will be noticed that the coefficient of friction of clean quartz is less than that of glass.

Steel and bismuth, when clean, show no change whatever in the friction over the range of temperature which was tried.

The result of these experiments with clean faces then is that the friction of a face of quartz, steel or bismuth, when thoroughly freed from adherent films, is sensibly independent of temperature over the range 15° to 110° C.

Table III.—Quartz.

Time.	Temperature (° C.).	μ.
0 minutes	16·5	0·770
45 ,,	16·5	0·770
120 ,,	110	0·765
145 ,,	110	0·765
210 ,,	18	0·763

Lubricated Faces.

Steel and quartz alone were used in these experiments; there is, of course, no reason to suppose that bismuth would have behaved differently.

Surfaces Flooded with Lubricant.—When the lubricant was fluid throughout the whole temperature range the friction was independent of temperature.

The following values were given, without sensible change, over the range 15° C. to 110° C. :—

Table IV.

Lubricant.	Steel.	Quartz.
	μ.	μ.
Undecane	0·34	0·49
Caprylic acid	0·20	0·306
Pelargonic acid	0·14	0·288
Butyl alcohol	0·39	0·545
Octyl ,, ...	0·29	0·457
Undecyl ,, ...	0·23	0·39

When the lubricant was solid over part of the range the effect of temperature was different below and above the melting point of the solid. The friction was always found to fall with rise of temperature up to the melting point. At this point there was a remarkable discontinuity, the friction falling to zero. When the lubricant was fully melted the friction suddenly reappeared at a higher level than before the discontinuity, and was constant over the remainder of the temperature range. When the temperature was allowed to fall from the highest point (110° C.) there was no change in friction until the melting point was again reached, when there was a sudden fall, but not to zero. Below this point it was not possible to go, because the slider became set fast in the solid mass of lubricant. These relations are illustrated in Table V, and by the curve in the diagram.

The lubricant was applied by placing a few crystals of the solid on the

plate in the chamber which had already been heated above the melting point. The slider was placed on the plate now covered by a layer of fluid lubricant and the chamber allowed to cool slowly. When at room temperature, the slider was lifted from the plate with the whole visible mass of lubricant attached to it, replaced, and observations of the friction were then taken.

Nonadecane, docosane, tetracosane, decoic acid, undecoic acid, palmitic acid, stearic acid, and cetyl alcohol were tried. It will be sufficient to give the figures for one of these :—

Table V.—Palmitic Acid on Quartz. Melting Point, 62° C.

Time.	Temperature (° C.).	μ.
45 minutes	19·0	0·163
65 ,,	28·4	0·140
90 ,,	34·2	0·121
110 ,,	39·8	0·098
145 ,,	48·5	0·063
160 ,,	54·5	0·038
195 ,,	59·8	0·021
210 ,,	62·0 (melting)	0·0
212 ,,	62·0 (liquid)	less
245 ,,	110	than
290 ,,	63	0·03
295 ,,	61·8 (solidifying)	

Cetyl alcohol on steel.
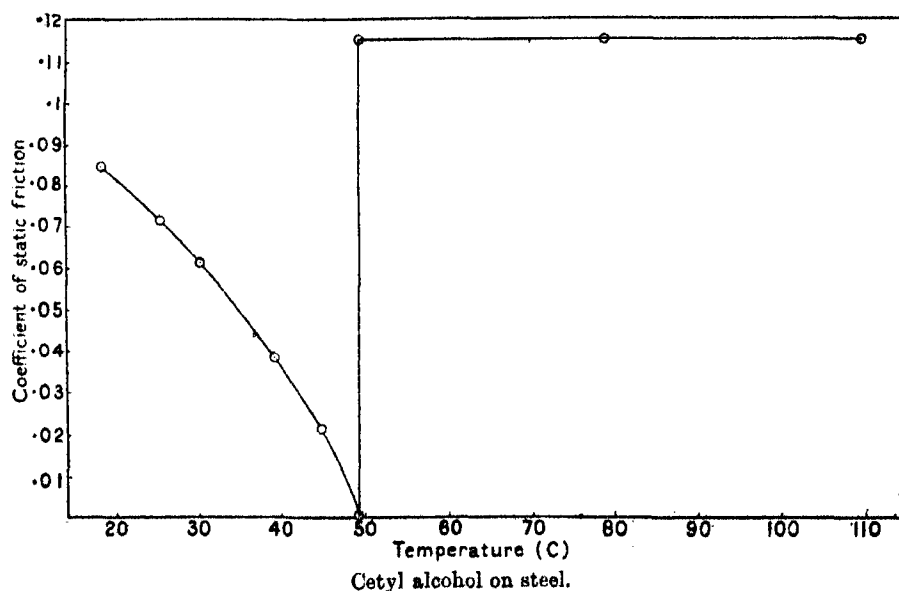
The discontinuity at the melting point would appear to be due to the fact that, when the lubricant is still solid, the friction that is measured is

that of the lubricant on itself. This might well be expected to fall with rise of temperature so near the melting point. This conclusion derives a certain amount of support from the fact that the coefficient of friction of a glass slider on the solid paraffin $C_{24}H_{50}$ is, at 16°, $\mu = 0.07$, whilst the coefficient of glass on glass lubricated by a film of this paraffin is $\mu = 0.325$. Above the melting point the friction, on the contrary, is that of solid faces, as modified by a primary film of the particular lubricant. In order to eliminate the friction of the lubricant on itself, films of insensible thickness were deposited on the faces from solutions in ether. The discontinuity now disappeared, and the friction became constant over the whole range, both when the temperature was rising and when it was falling, and we may therefore conclude that, over the range of temperature 15° to 110° C., the friction of quartz and of steel, lubricated with normal paraffins and the related normal acids and alcohols, is sensibly independent of temperature.

Table VI.

Lubricant.	Temperature (° C.).	
	Steel.	
$C_{19}H_{40}$	15·6–110	0·179
$C_{22}H_{46}$	17·3–110	0·110
$C_{24}H_{50}$	17·0–110	0·068
Cetyl alcohol	16·5–110	0·1143
Decoic acid	15·0– 75	0·075
Undecoic acid...........	15·0– 80	} Negligible—glides with weight of scale pan.
Palmitic „	16·5–110	
Stearic „	17·0–110	
	Quartz.	
$C_{19}H_{40}$	15·0–110	0·324
$C_{22}H_{46}$	15·8–110	0·26
$C_{24}H_{50}$	16·5–110	0·23
Cetyl alcohol	19·0–110	0·276
Decoic acid..............	17·2–110	0·18
Undecoic acid...........	16·5–110	0·114
Palmitic „	16·5–110	} Glides with weight of scale pan.
Stearic „	18·8–110	
Myristic „	18·0–110	

The curious fact that there is no static friction at the melting point of a lubricant when the faces are flooded with it is not so readily explained. The phenomenon is observed when the lubricant is partly solid and partly melted. We may therefore picture to ourselves the solid faces, each covered by its adherent film, and separated during melting by a mixture of solid and

fluid lubricant, and the latter is continually being supplied at the expense of the former. Under these conditions the friction would be fluid friction, and therefore static friction would be absent; and the friction of the solid faces, as lubricated by the particular lubricant, would not reappear until melting was complete and all the fluid squeezed out by the weight of the slider, leaving the solid faces separated by two primary films of lubricant, as described in the earlier paper. The fact that the static friction reappears instantly and at full value confirms the view there taken that solid friction does not change gradually to fluid friction, but that the one changes to the other abruptly at a certain critical thickness of the film. The state of the material in these lubricating films is determined by the attraction field of the solid as well as by the mutual attraction of the atoms and molecules of which it is composed. Since there is no change in the curve friction/temperature at the melting point of the lubricant, we may suppose that the former is more important than the latter. The fact, known since Leslie's time, that heat is liberated when a solid is wetted by a fluid, shows that the degree of freedom of a molecule in these films is less than that of one in the interior of a fluid mass of the same lubricant.

The curves connecting static friction with molecular weight, which were given in the last paper, cut the base line; that is to say, above a molecular weight which is different for each chemical series, static friction should vanish. More careful measurements made since the last paper was written show that this actually is so when the lubricant is present only as a film of insensible thickness. Then the slider moved with the smallest weight which could be applied, namely, 0·7 grm. It moved slowly, as might be expected, since the accelerating force was so small—the observed rate being of the order 0·4 mm. per hour.

When the lubricant is present in excess there frequently is resistance to movement due to surface tension, for consider a small drop symmetrically disposed about the area of contact between slider and plate. Movement of the slider will increase the area of the interfaces between the drop and air and the drop and the plate. In certain cases this absorbs work. For example, a steel slider in a small drop of melted palmitic acid on a steel plate needed a weight of 3·6 grm. to move it, when the drop was smeared about the plate a weight of 0·9 grm. was sufficient, but when the acid was present on the surfaces only as a film of insensible thickness the weight of the scale pan (0·7 grm.) alone sufficed to make the slider glide slowly.

On the Lateral Vibrations of Bars of Conical Type.

By Dorothy Wrinch, D.Sc., Girton College, Cambridge.

Introduction.

This paper contains a discussion of the lateral vibrations of a thin conical bar of circular section, which has its tip free. By means of a discussion of the roots of certain equations containing Bessel functions of the second and third orders, both of real and of imaginary argument, the frequencies and nodal arrangement associated with the first three tones are investigated, in the case when the base of the bar is clamped.

The lateral vibrations of conical bars of circular section were first treated by Kirchhoff,[*] in 1879. In his investigations, Kirchhoff was concerned with the case of a bar with its tip free and its base clamped, and he limited himself to a discussion of the period associated with the gravest tone, and considered neither the higher periods nor the positions of the nodes associated with them. J. W. Nicholson,[†] in the course of an investigation of the lateral vibrations of certain types of bars of variable section, discussed the case of a double cone (consisting of two equal cones placed base to base,) vibrating with both tips free, and discussed the periods and nodal ratios associated with the first three symmetrical tones. His results, however, throw no light on the question of the vibrations of a conical bar with a clamped base, owing to the peculiar nature of the conditions at the centre.

The present paper, in addition, contains an investigation of the periods of the higher tones, and of the arrangement of the nodes associated with these tones. The discussion gives for the case of a clamped-free bar of conical type the results which correspond to those given by Lord Rayleigh,[‡] and Seebeck,[§] and Donkin, for a bar of uniform cross section. General characteristics are worked out of the nodal arrangement in the higher tones when the tip is free, and nothing is known about the conditions at the base.

In the discussion of the higher tones of the free-clamped bar, the method

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[*] 'Sitz. der Akad. zu Berlin,' p. 815 (1879).

[†] 'Proc. Roy. Soc.,' A, p. 506 (1917).

[‡] 'Theory of Sound,' vol. 1, p. 286.

[§] 'Abhandlungen d. Math. Phys. Classe d. k. Sächs. Gesellschaft d. Wissenschaften, Leipzig, 1852.

is used of determining the equation which gives the period by a generalised hypergeometric series of the form

$$f(a, b, c; x) = 1 - x/1 \cdot 1 + a \cdot 1 + b \cdot 1 + c$$
$$+ x^2/1 \cdot 2 \cdot 1 + a \cdot 2 + a \cdot 1 + b \cdot 2 + b \cdot 1 + c \cdot 2 + c - \ldots,$$

and introducing the asymptotic expansion[*] of this series for large values of x, which has not hitherto been employed in physical problems. The first term alone of this expansion, which is a multiple of

$$\cos (4x^{1/4} \sin \pi/4 - \pi (a + b + c + 3/2)/4),$$

when equated to zero, gives the periods with an accuracy of about one part in 100 in the case of the third tone, and with progressively greater accuracy for the higher tones.

The investigation yields the following result :—

In the lateral vibrations of a conical bar vibrating with a free end, whatever the conditions at the base may be, the nodes in the nth tone occur at intervals of order $1/n$ in the neighbourhood of the base, and at intervals of order $1/n^2$ in the neighbourhood of the tip.

The importance of vibrations in morphology has been pointed out by Prof. Dendy,[†] in the course of an investigation into the positions of siliceous deposits found on sponge spicules ; and, indeed, the investigation of Prof. Nicholson, already referred to, was undertaken with the purpose of testing the suggestion of Prof. Dendy, that these deposits occur at the nodes of the spicules, regarded as vibrating rods. The high degree of agreement obtained gives this suggestion a large measure of probability. In the types of physical problems which have been discussed from this point of view, the lower notes have, for the most part, been the important ones. With further applications to problems of morphology in view, it was deemed worth while to include in this paper, not only a full discussion of the lower tones, but also a general account of the nodal arrangement associated with the higher tones.

The Equation of Motion.

Let the bar be formed by the revolution of the line $y = Ax$ about the axis of x, the thick extremity of the bar being given by the plane $x = 1$. The displacement at any point x is y, E is the modulus of elasticity and ρ the density of the material. In the case of a thin bar, in which the rotatory

* E. W. Barnes, 'Phil. Trans.,' A, vol. 206, p. 297 (1906) ; D. M. Wrinch, 'Phil. Mag.,' p. 161 (1921).

† Presidential Address to the Quekett Microscopical Club, 'Journ. Q.M.C.,' p. 231 (1917) ; 'Proc. Roy. Soc.,' B, p. 573 (1917).

inertia can be neglected,[*] the equation of motion during a lateral vibration is well known to be

$$\frac{\partial^2}{\partial x^2}\left(\tfrac{1}{4}\pi E A^4 x^4 \frac{\partial^2 y}{\partial x^2}\right)+\pi\rho A^2 x^2 \frac{\partial^2 y}{\partial t^2}=0.$$

For a vibration of period $2\pi/p$,

$$\frac{\partial^2 y}{\partial t^2}=-p^2 y,$$

and therefore

$$\frac{\partial^2}{\partial x^2}\left(x^4 \frac{\partial^2 y}{\partial x^2}\right)=ax^2 y,$$

or

$$\frac{\partial^2}{\partial z^2}\left(z^4 \frac{\partial^2 y}{\partial z^2}\right)=z^2 y,$$

if we introduce a new variable z, defined by the equations,

$$z=qx, \qquad q^2=4\rho p^2/EA^2.$$

This fourth order differential equation can conveniently be exhibited in the form

$$\vartheta(\vartheta-1)z^2\vartheta(\vartheta-1)y=z^4 y,$$

where $\vartheta=z\partial/\partial z,$

or $(\vartheta+2)(\vartheta+1)\vartheta(\vartheta-1)y=z^2 y.$

When it is written in the form

$$[z^{-1}\vartheta(\vartheta+2)]^2 y=y,$$

two solutions of it are seen to be

$$y=\alpha[1-z/1.3+z^2/1.3.2.4-\dots],\quad \gamma[1+z/1.3+z^2/1.3.2.4+\dots],$$
$$=AJ_2(2\sqrt{z})/z, \qquad CI_2(2\sqrt{z})/z.$$

The general solution is therefore evidently

$$y=AJ_2(2\sqrt{z})/z+BY_2(2\sqrt{z})/z+CI_2(2\sqrt{z})/z+DK_2(2\sqrt{z})/z,$$

where Y and K are the Bessel functions of the second kind.

The constants A, B, C, D, are determined by the conditions of support of the bar. In the case under consideration the end $z=0$ is free, and the shearing stress and bending moment, which are respectively proportional to

$$z^4\,\partial^2 y/\partial z^2, \qquad \frac{\partial}{\partial z}\left(z^4 \frac{\partial^2 y}{\partial z^2}\right),$$

must vanish. Since the functions Y and K are logarithmically infinite near $z=0$, B and D must vanish. Further at the thick end, at which $z=ql=\beta$ the conditions for a clamped end require that y and dy/dx should vanish.

Since

$$\frac{d}{dz} z^{-1} J_2(2\sqrt{z}) = -z^{-3/2} J_3(2\sqrt{z}), \quad \frac{d}{dz} z^{-1} I_2(2\sqrt{z}) = z^{-3/2} I_3(2\sqrt{z}),$$

these conditions can be written

$$A J_2(2\sqrt{\beta}) + C I_2(2\sqrt{\beta}) = 0,$$

$$A J_3(2\sqrt{\beta}) - C I_3(2\sqrt{\beta}) = 0,$$

yielding the equation

$$J_2(2\sqrt{\beta}) I_3(2\sqrt{\beta}) + J_3(2\sqrt{\beta}) I_2(2\sqrt{\beta}) = 0, \qquad (1)$$

as the period equation determining β.

This period equation can easily be thrown into the form used by Kirchhoff,[*] namely,

$$0 = 1/2!\,3! - \beta^2/1!\,3!\,5! + \beta^4/2!\,4!\,7! - \beta^6/3!\,5!\,9! + \dots.$$

We may write the period equation in a slightly more convenient form by employing Bessel functions of the first and second orders, instead of those of the second and third orders. For by the well known recurrence formulæ for these functions,

$$J_1(x) + J_3(x) = 4 J_2(x)/x, \qquad I_1(x) - I_3(x) = 4 I_2(x)/x.$$

And the period equation becomes, when we substitute for J_3 and I_3,

$$J_2(2\sqrt{\beta}) I_1(2\sqrt{\beta}) = J_1(2\sqrt{\beta}) I_2(2\sqrt{\beta}).$$

The first ten roots of this equation were obtained by Airey, who encountered the same equation in the course of an investigation on the vibrations of circular plates. It is a striking fact that this equation occurs in such very different problems. Quoting the first three roots from Airey's[†] paper,

$$2\sqrt{\beta} = 5 \cdot 906,\ 9 \cdot 197,\ 12 \cdot 402,$$

and returning to the definition of β, we find that the corresponding periods are given by

$$2\pi/p = 16\pi l^2/d \cdot \sqrt{\frac{\rho}{E}} (5 \cdot 906,\ 9 \cdot 197,\ 12 \cdot 402)^{-2}.$$

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[*] *Loc. cit.*, p. 826. Kirchhoff gave the first root as $\beta = 8 \cdot 718$. A more accurate value is $8 \cdot 7202$. P. F. Ward, following Kirchhoff, has also investigated this period equation, which occurred in the course of a discussion of the lateral vibrations of a pyramidal bar of square section, vide 'Phil. Mag.,' p. 85 (1913).

[†] 'Proc. Phys. Soc. London,' p. 225 (1911).

The Nodal Positions.

The displacement of any point on the rod is given by

$$y = AJ_2(2\sqrt{z}) + CI_2(2\sqrt{z})$$

where the ratio of A to C has now been implicitly determined in terms of the period associated with the tone under consideration. Thus

$$AJ_2(2\sqrt{\beta}) + CI_2(2\sqrt{\beta}) = 0.$$

Hence the displacement is a multiple of

$$J_2(2\sqrt{z})\,I_2(2\sqrt{\beta}) - I_2(2\sqrt{z})\,J_2(2\sqrt{\beta}).$$

The equation determining the positions of the nodes, at which the displacement is zero, is therefore

$$J_2(2\sqrt{z})/I_2(2\sqrt{z}) = J_2(2\sqrt{\beta})/I_2(2\sqrt{\beta}). \tag{2}$$

Associated with the first tone, in which $2\sqrt{(\beta)} = 5\cdot906$, there is only one root of this equation which is not larger than β, namely, β itself. The clamped end is naturally the only node. In the next tone, in which $2\sqrt{(\beta)} = 9\cdot197$, the equation becomes

$$J_2(2\sqrt{z})/I_2(2\sqrt{z}) = J_2(9\cdot197)/I_2(9\cdot197) = 0\cdot0001752.$$

In order to solve the equation

$$J_2(2\sqrt{z})/I_2(2\sqrt{z}) = a, \tag{3}$$

where, as is always the case in these applications, a is very small, since $I_2(2\sqrt{\beta})$ is large, we have, writing $2\sqrt{z} = x$,

$$J_2(x) = aI_2(x)$$

and an approximation to the roots can be obtained by considering the roots of the equation

$$J_2(x) = 0. \tag{4}$$

For, putting

$$x = \alpha + \epsilon$$

where α is a root of the equation $J_2(x) = 0$, and neglecting ϵ^2 we get

$$J_2(\alpha) + \epsilon J_2{}'(\alpha) = aI_2(\alpha) + a\epsilon I_2{}'(\alpha);$$

or, since $J_2(\alpha) = 0$,

$$\epsilon = aI_2(\alpha)/(J_2{}'(\alpha) - aI_2{}'(\alpha))$$
$$= 2aI_2(\alpha)/[J_1(\alpha) - J_3(\alpha) - a(I_1(\alpha) + I_3(\alpha))].$$

But $J_1(\alpha) = -J_3(\alpha)$ since $J_2(\alpha) = 0$; therefore

$$\epsilon = 2aI_2(\alpha)/[2J_1(\alpha) - a(I_1(\alpha) + I_3(\alpha))]$$

and evidently this value of ϵ is smaller for the earlier zeros of J_2 than for the later ones. For example, in the case of the second tone, with a node at the

clamped end, corresponding to the value $x = 9 \cdot 197$, and another node in the bar, the first root of $J_2(x) = 0$, namely, $x = 5 \cdot 135$, gives a close approximation to the first root of the equation (3).

For putting $$\alpha = 5 \cdot 135$$

we can determine readily from tables and recurrence formulæ that
$$J_1(\alpha) = -J_3(\alpha) = -0 \cdot 3396,$$
$$I_1(\alpha) = 27, \qquad I_3(\alpha) = 11,$$
and since in this case
$$a = 0 \cdot 000175$$
we find that
$$\epsilon = -0 \cdot 004$$
as a first correction. Thus,
$$x = 5 \cdot 131.$$

The approximation can be continued in the same manner, but it is not in this case necessary. The node is therefore at a distance from the tip, which is in the ratio
$$z/\beta = (5 \cdot 131/9 \cdot 197)^2 = 0 \cdot 304$$
to the length of the bar.

For the third tone, which will have two nodes in the bar, in addition to the node at the clamped end, we have $2\sqrt{\beta} = 12 \cdot 402$, and the equation for the nodes, if $x = 2\sqrt{z}$, is
$$J_2(x)/I_2(x) = J_2(12 \cdot 402)/I_2(12 \cdot 402) = -0 \cdot 159/23545 = -0 \cdot 00000675.$$

There will be roots of this equation in the neighbourhood of $5 \cdot 135$ and $8 \cdot 417$, the first two zeros of J_2. For the root near $5 \cdot 135$, the necessary correction to the value $5 \cdot 135$ is effectively, for all tones, in the ratio of the corresponding values of a, and thus becomes, for the third tone,
$$\epsilon = aI_2(5 \cdot 135)/J_1(5 \cdot 135) = 0 \cdot 004 (0 \cdot 0^5675)/0 \cdot 0^3175$$
and is in general negligible. The value of x for the first root of the nodal equation for the third tone is therefore $5 \cdot 135$ effectively. In the next case,
$$a = 0 \cdot 0^6273,$$
and therefore the first root is again effectively $5 \cdot 135$. The node nearest to the tip, therefore, in all tones corresponds to practically the same value of x. The mutual separations of the second roots and third roots of the nodal equations become progressively larger.

The other node in the third tone will be given by a value of x in the neighbourhood of $8 \cdot 417$. For argument so large as 8 the function I_2 is effectively given by the asymptotic expansion
$$I_2(x) = e^x/(2\pi x)^{1/2}$$
and our equation is effectively,
$$x^{1/2} J_2(x) e^{-z} = a/\sqrt{(2\pi)}.$$

Although interpolation is not easily accomplished with this equation, on account of the exponential nature of I_2, we find that it gives excellent results in this and similar cases when logarithms are taken. The solution is quickly found to be

$$x = 8\cdot401.$$

The corresponding nodal ratio is

$$z/\beta = (8\cdot401/12\cdot402)^2 = 0\cdot458.$$

Thus the nodal ratios in this tone are

$$0\cdot171, \quad 0\cdot458, \quad 1.$$

A general discussion of the equation

$$J_2(2\sqrt{z})/I_2(2\sqrt{z}) = J_2(2\sqrt{\beta})/I_2(2\sqrt{\beta})$$

is given later, with a more general investigation of the nodal arrangements in the higher tones than can be obtained from these numerical considerations.

The Higher Tones.

Lord Rayleigh,[*] in the course of his investigation into the lateral vibrations of a free-clamped bar of uniform cross-section, quoted a well known formula, due to Seebeck and Donkin, for the positions of the nodes in the higher tones. Seebeck (*loc. cit.*) and Donkin proved that the nodal ratios in the nth tone, measuring from the free end, are given by

$$1\cdot3222/(4n-2), \quad 4\cdot9820/(4n-2), \quad 9\cdot0007/(4n-2), \quad 13/(4n-2),$$
$$17/(4n-2), \ldots (4n-10\cdot993)/(4n-2),$$
$$(4n-7\cdot0175)/(4n-2) \ldots (4n-2)/(4n-2).$$

Lord Rayleigh found the corresponding ratios for the free-free bar to be

$$1\cdot3222/(4n-2), \quad 4\cdot9820/(4n-2), \quad 9\cdot0007/(4n-2), \quad 13/(4n-2),$$
$$17/(4n-2), \quad 21/(4n-2), \ldots (4n-3)/(4n-2).$$

We proceed to obtain a corresponding formula for the bar of conical type.

The Period Equation.

Referring again to the equation (1), we notice that the period equation is formed by eliminating the constants A and C between the equations

$$y = AJ_2(2\sqrt{z})/z + CI_2(2\sqrt{z})/z = 0, \tag{5}$$

$$\partial y/\partial z = A\partial/\partial z\,(J_2(2\sqrt{z})/z) + C\partial/\partial z\,(I_2(2\sqrt{z})/z) = 0. \tag{6}$$

The period equation is therefore of the form,

$$Y = y_1 y_2' - y_2 y_1' = 0, \tag{7}$$

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[*] *Loc. cit.*, p. 286.

where $\quad y_1 = J_2(2\sqrt{z})/z = 1 - z/1.3 + z^2/1.3.2.4 - \dots$

and satisfies the equation

$$\vartheta(\vartheta + 2)\,y_1 = -zy_1 \qquad (8)$$

where, again, $\vartheta = z\,\partial/\partial z$, and

$$y_2 = I_2(2\sqrt{z})/z = 1 + z/1.3 + z^2/1.3.2.4 + \dots$$

and satisfies the equation

$$\vartheta(\vartheta + 2)\,y_2 = zy_2. \qquad (9)$$

We now proceed to find the differential equation satisfied by Y.

We have $\qquad y_1\,\vartheta y_2 - y_2\,\vartheta y_1 = z\mathrm{Y}.$

Applying the operator $(\vartheta + 2)$ to both sides, we obtain

$$y_1\,\vartheta(\vartheta + 2)\,y_2 - y_2\,\vartheta(\vartheta + 2)\,y_1 = z(\vartheta + 3)\,\mathrm{Y}$$

which with the help of equations (8), (9), becomes

$$y_1 y_2 = \tfrac{1}{2}(\vartheta + 3)\,\mathrm{Y}.$$

Next applying the operator $\vartheta(\vartheta + 2)$, we get

$$y_1\,\vartheta(\vartheta + 2)\,y_2 + y_2\,\vartheta(\vartheta + 2)\,y_1 + 2\vartheta y_1\,\vartheta y_2 = \tfrac{1}{2}\vartheta(\vartheta + 2)(\vartheta + 3)\,\mathrm{Y},$$

or, again, using the equations (8), (9),

$$\vartheta y_1\,\vartheta y_2 = \tfrac{1}{4}\vartheta(\vartheta + 2)(\vartheta + 3)\,\mathrm{Y}.$$

Applying the operator ϑ, the equation yields

$$\vartheta^2 y_1\,\vartheta y_2 + \vartheta y_1\,\vartheta^2 y_2 = \tfrac{1}{4}\vartheta^2(\vartheta + 2)(\vartheta + 3)\,\mathrm{Y}.$$

Adding to both sides $4\vartheta y_1\,\vartheta y_2$ we obtain the equation

$$\vartheta(\vartheta + 2)\,y_1\,\vartheta y_2 + \vartheta(\vartheta + 2)\,y_2\,\vartheta y_1 = \tfrac{1}{4}\vartheta^2(\vartheta + 2)(\vartheta + 3)\,\mathrm{Y} + \vartheta(\vartheta + 2)(\vartheta + 3)\,\mathrm{Y},$$

or $\qquad z(y_2\,\vartheta y_1 - y_1\,\vartheta y_2) = \tfrac{1}{4}\vartheta(\vartheta + 2)(\vartheta + 3)(\vartheta + 4)\,\mathrm{Y},$

giving finally the fourth order equation for Y,

$$\vartheta(\vartheta + 2)(\vartheta + 3)(\vartheta + 4)\,\mathrm{Y} + 4z^2\mathrm{Y} = 0. \qquad (10)$$

The Asymptotic Expansion of the Series for Determining the Period.

The expression of the fourth order equation for Y in terms of the operator ϑ enables us to write down series solutions at once. Since the particular solution we need begins with a constant term, it is clearly

$$\mathrm{Y} = a(1 - 4z^2/2.4.5.6 + 4z^{2\cdot2}/2.4.5.6.4.6.7.8. - \dots)$$

$$= a(1 - (\tfrac{1}{2}z)^2/1.2.5/2.3 + (\tfrac{1}{2}z)^4/1.2.5/2.3.2.3.7/2.4 - \dots).$$

This series is of the generalised hypergeometric type with four denominators, namely,

$$1 - x/1.1 + a.1 + b.1 + c + x^2/1.2.1 + a.2 + a.1 + b.2 + b.1 + c.2 + c - \dots$$

and the asymptotic expansion of the series for large values of x is known to be[*]

$$\frac{\Gamma(1+a)\,\Gamma(1+b)\,\Gamma(1+c)}{2\,(2\pi)^{3/2}}\left\{\cos\left(4x^{1/4}\sin\pi/4-\pi s_4/4\right)\left[1+\alpha_2/x^{1/2}+\alpha_4/x+\ldots\right]\right.$$

$$\left.+\sin\left(4x^{1/4}\sin\pi/4-\pi s_4/4\right)\left[\frac{\alpha_1}{x^{1/4}}+\frac{\alpha_3}{x^{3/4}}+\ldots\right]\right\}$$

where

$$s_4 = a+b+c+3/2.$$

Taking, in the first instance, only the term of largest order, we may consider the roots of the equation

$$\cos\left(4x^{1/4}\sin\pi/4-\pi s_4/4\right)=0,$$

which may be written

$$4x^{1/4}\sin\pi/4-\pi s_4/4=(2r-1)\,\pi/2,\qquad(r=1,\,2,\,\ldots).$$

In the particular series under discussion,

$$x=z^2/4,\qquad s_4=6,$$

and the corresponding roots will be

$$2z^{1/2}=(r+1)\,\pi,\qquad(r=1,\,2,\,\ldots),$$

The first ten roots of the period equation are already known to be

$$x = 5\cdot906,\ 9\cdot197,\ 12\cdot402,\ 15\cdot579,\ 18\cdot745,$$

$$21\cdot901,\ 25\cdot055,\ 28\cdot205,\ 31\cdot354,\ 34\cdot502,$$

or, as they may be written more conveniently,

$$x/\pi = 1\cdot8807,\ 2\cdot9277,\ 3\cdot9478,\ 4\cdot9591,\ 5\cdot9660,$$

$$6\cdot9714,\ 7\cdot9751,\ 8\cdot9781,\ 9\cdot9804,\ 10\cdot983,$$

whereas the roots obtained by using the first term of the asymptotic expansion are

$$x/\pi = 2,\ 3,\ 4,\ 5,\ 6,\ 7,\ 8,\ 9,\ 10,\ 11,\ \ldots.$$

Our approximation, therefore, gives even the fourth root with an error of less than one part in 100. The error in the higher roots rapidly becomes smaller and is less than $1\cdot5$ in 1000 in the case of the tenth root.

Consequently, the periods associated with the first ten tones are given by

$$2\pi/p = 16l^2/d\pi\ .\ \sqrt{\frac{\rho}{\mathrm{E}}}\,[1\cdot8807,\ 2\cdot9277,\ 3\cdot9478,\ 4\cdot9591,\ 5\cdot9660,$$

$$6\cdot9714,\ 7\cdot9751,\ 8\cdot9781,\ 9\cdot9804,\ 10\cdot985]^{-2},$$

and in general the period of the $n-1$th tone, when $n \geq 11$, is given, with an error of less than three parts in 1000, by

$$2\pi/p = 16l^2/n^2\pi d\ .\ \sqrt{\frac{\rho}{\mathrm{E}}}.$$

[*] *Loc. cit.*, Barnes, Wrinch.

The Nodal Positions in the Higher Tones.

The equation determining the nodal ratios in the various tones is

$$J_2(2\sqrt{z})/I_2(2\sqrt{z}) = J_2(2\sqrt{\beta})/I_2(2\sqrt{\beta}) = a$$

when the value of β associated with the particular tone under consideration is inserted. We may write for convenience

$$x = 2\sqrt{z}, \qquad b = 2\sqrt{\beta},$$

and deal with the equation

$$J_2(x)/I_2(x) = J_2(b)/I_2(b) = a. \tag{11}$$

The values of b associated with the various tones are

$$b = 5\cdot906, \, 9\cdot197, \, 12\cdot402, \, 15\cdot579, \, 18\cdot745,$$

$$21\cdot901, \, 25\cdot955, \, 28\cdot205, \, 31\cdot154, \, 34\cdot502,$$

$$b/\pi = 1\cdot881, \, 2\cdot928, \, 3\cdot948, \, 4\cdot959, \, 5\cdot966, \, 6\cdot971, \, 7\cdot975, \, 8\cdot978, \, 9\cdot980, \, 10\cdot983,$$

and the corresponding values of $J_2(b)$ are alternately negative and positive. Thus in the first, third, ..., $2n-1$th tones, in the equation for the nodal distances, a is negative. In the other tones $J_2(b)$ and consequently a is positive.

The curve $$y = J_2(x)/I_2(x),$$

is of an oscillatory type and cuts the axis of x in a series of points

$$x = \alpha_1, \, \alpha_2, \, \alpha_3, \, \ldots \, \alpha_r, \, \alpha_{r+1}, \, \ldots$$

which are the roots of the equation, $J_2(x) = 0$. The first three are given by

$$x = 5\cdot135, \, 8\cdot417, \, 11\cdot620,$$

$$x/\pi = 1\cdot597, \, 2\cdot679, \, 3\cdot699,$$

and the higher ones more and more closely by

$$x/\pi = n + 3/4, \qquad (n = 4, 5 \ldots).$$

The amplitude decreases rapidly as x increases. From these characteristics of the curve $y = J_2(x)/I_2(x)$ it follows that the values of x which satisfy the equation occur in pairs within the divisions

$$(0 \, \alpha_1), \qquad (\alpha_2 \, \alpha_3), \quad \ldots \quad (\alpha_{2m} \, \alpha_{2m+1}), \quad \ldots,$$

or within the divisions

$$(\alpha_1 \, \alpha_2), \qquad (\alpha_3 \, \alpha_4), \quad \ldots \quad (\alpha_{2m+1} \, \alpha_{2m+2}), \quad \ldots,$$

where, as before, the α's are the roots of the equation $J_2(x) = 0$. Hence, in the $(n-1)$th tone, supposing first that n is odd (so that a is positive,) the roots can be represented by

$$x = \alpha_1 - \lambda_1(n), \qquad \alpha_2 + \lambda_2(n), \qquad \alpha_3 - \lambda_3(n), \, \ldots \, \alpha_n + \lambda_n(n).$$

In this expression for the roots, the quantities λ are all positive. If n is even the roots can be represented in the same way with all the signs of the λ's reversed. It is hardly practicable to find the values of the λ's associated with the higher tones to any specified degree of accuracy. We shall instead deduce general properties of the sequences $\lambda_1, \lambda_2, ..., \lambda_r$, associated with each tone.

The fact that the amplitude of the curve

$$y = J_2(x)/I_2(x)$$

decreases in each succeeding division implies that the quantities

$$\lambda_1(r), \lambda_2(r), ..., \lambda_r(r)$$

form a steadily increasing sequence. For in order that x may satisfy the equation

$$J_2(x)/I_2(x) = a$$

where a is not zero although it is small, in each division x will have to move further away from the points

$$\alpha_1, \quad \alpha_2, \quad ... \quad \alpha_r,$$

which define the divisions and satisfy the equation

$$J_2(\alpha) = 0.$$

The distance between roots belonging to the same division becomes smaller and, at the same time, the distance between roots belonging to different divisions becomes larger. The pairing of the roots, consequently, becomes increasingly marked.

We therefore have the result,

$$0 < \lambda_1(r) < \lambda_2(r) < \lambda_3(r) \, ... \, < \lambda_r(r).$$

And we observe that as we consider the roots of the equations associated with higher tones, the corresponding λ's increase. Further, the upper limits associated with the first, second, ..., rth tones are given respectively by the differences between the first, second, ..., rth roots of the equations

$$J_2(x)/I_2(x) = a, \qquad J_2(x) = 0,$$

and we therefore have

$$0 < \lambda_1(r) < \lambda_2(r) \, ... \, < \lambda_r(r) < (b_r - a_r)$$

where b_r and a_r represent the rth roots of these equations. The higher roots of these equations tend to the form $(r+1)\pi$ and $(r+3/4)\pi$ respectively, so that $b_r - a_r$ tends to $\pi/4$.

We collect together the values of x associated with the first three tones, which we have already investigated in an earlier section of the paper.

<div align="center">

First tone, 5·906,

Second tone, 5·131, 9·197,

Third tone, 5·135, 8·402, 12·402,

</div>

and the first three roots of the equation $J_2(x) = 0$ are

$$5·135, \quad 8·417, \quad 11·620;$$

the corresponding values of the λ's are exhibited in the subjoined table

	λ_1.	λ_2.	λ_3.
First tone	0·771		
Second tone............	0·004	0·780	
Third tone	0·000	0·015	0·782

We may, in addition, exhibit the behaviour of the first and last λ's associated with each tone.

Number of tone.	$\lambda_1(r)$.	$\lambda_r(r)$.
1	0·771	0·771
2	0·004	0·780
3	0·000	0·782
4	0·000	0·783
5	0·000	0·785

The convergence of $\lambda_1(r)$ to zero and the convergence of $\lambda_r(r)$ to $\pi/4$ is plainly seen.

The Nodal Ratios.

Let b_m represent the mth root of the period equation

$$J_2(b)/I_2(b) = J_3(b)/I_3(b),$$

and $_m x_n$ the mth root of the nodal equation associated with the nth tone, namely,

$$J_2(x)/I_2(x) = J_3(b_n)/I_3(b_n). \tag{12}$$

We will denote the ratio of the distance of the mth node in the nth tone from the tip to the whole length of the bar by $_m r_n$. Then, as before, the nodal ratios will be given by the formula

$$_m r_n = (_m x_n/b_n)^2.$$

Now, we have already shown that in the case of the roots of the nodal equation there exists a sequence

$$\lambda_1(n), \quad \lambda_2(n), \quad \dots \quad \lambda_n(n),$$

which is such that

$$0 < \lambda_1(n) < \lambda_2(n) \dots < \lambda_n(n) < \frac{\pi}{4}$$

which enables us to express the roots $_m x_n$ in the form

$$_m x_n = \alpha_m \pm \lambda_m(n),$$

the upper or lower signs being taken, according as $n - m$ is even or odd. As before, we write α_m for the mth zero of the function $J_2(x)$. If we put

$$_m R_n = (\alpha_m / b_n)^2$$

it is evident that the nodal ratios interlace with the ratios $_m R_n$ in such a way that

$$_n r_n >_n R_n >_{n-1} R_n >_{n-1} r_n >_{n-2} r_n >_{n-2} R_n >_{n-3} R_n \dots .$$

The nodal ratios, in fact, occur in pairs within the successive pairs

$$(_{n-1} R_n, \quad _{n-2} R_n), \qquad (_{n-3} R_n, \quad _{n-4} R_n) \dots .$$

Further, the ratios $_m r_n$ approach the ratios $_m R_n$ more and more closely as m decreases. We have already seen that the difference between

$$(\alpha_1 / b_n)^2$$

and the nodal ratio

$$(_1 x_n / b_n)^2$$

decreases as n increases, and is indeed less than one part in 5000 when $n = 3$. We found also that the ratio

$$(\alpha_2 / b_n)^2$$

differs from the nodal ratio

$$(_2 x_n / b_n)^2$$

by only one part in 500 for $n = 3$. It is clear, therefore, that when n is sufficiently large a good approximation to the smaller nodal ratios will be given by the ratios

$$(\alpha_1 / b_n)^2, \qquad (\alpha_2 / b_n)^2, \qquad (\alpha_3 / b_n)^2 \dots .$$

In the case of a bar of unit length, the intervals between two nodes in the neighbourhood of the tip is evidently always of order $1/n^2$. For the earlier values of the α's are given by

$$\alpha/\pi = 1{\cdot}597, 2{\cdot}679, 3{\cdot}699, 4{\cdot}710, 5{\cdot}717, 6{\cdot}721, 7{\cdot}725, 8{\cdot}730, 9{\cdot}731.$$

Further $$b_n = (n+1)\pi + 0(1/n).$$

The nodal ratios in the neighbourhood of the tip are consequently given by

$$(1{\cdot}597/n)^2, \qquad (2{\cdot}679/n)^2, \qquad (3{\cdot}699/n)^2, \dots ,$$

if we neglect terms of order $1/n^3$.

When we pass to nodal ratios in which m is comparable with n, we have

$$(\alpha_{n-1}-\pi/4)^2/b_n{}^2 \quad < \quad {}_{n-1}r_n \quad < \quad (\alpha_{n-1}/b_n)^2,$$

$$(\alpha_{n-2}+\pi/4)^2/b_n{}^2 \quad > \quad {}_{n-2}r_n \quad > \quad (\alpha_{n-2}/b_n)^2,$$

$$(\alpha_{n-3}-\pi/4)^2/b_n{}^2 \quad < \quad {}_{n-3}r_n \quad < \quad (\alpha_{n-3}/b_n)^2, \ldots .$$

These results specify the nodal ratios within

$$\frac{\pi}{4}(2\alpha_{n-1}-\pi/4)/b_n{}^2.$$

We can easily deduce that the intervals between consecutive nodes in the neighbourhood of the base are of order $1/n$, in the case of a bar of unit length.

To obtain the values of the nodal ratios to any degree of accuracy which is required, we employ the method of a previous section. As a first approximation to the roots of the equation

$$J_2(x)/I_2(x) = J_2(b_n)/I_2(b_n) = a_n$$

we obtained the result

$$_m x_n = \alpha_m + {}_n\epsilon_m,$$

with $\qquad {}_n\epsilon_m = a_n I_2(\alpha_m)/(J_1(\alpha_m) - a_n(I_1(\alpha_m) + I_3(\alpha_m)))$.

Since

$$\alpha_m = (m+3/4)\pi + 0(1/m),$$

$$b_n = (n+1)\pi + 0(1/n),$$

$$I_1(\alpha_m) = \frac{e^{(m+3/4)\pi}}{\sqrt{2\pi^2 m}}\left[1+0\left(\frac{1}{m}\right)\right] = I_3(\alpha_m),$$

$$J_1(\alpha_m) = \sqrt{\frac{2}{\pi^2 m}}\cos m\pi\left[1+0\left(\frac{1}{m}\right)\right],$$

and

$$a_n = 2e^{-(n+1)\pi}\cos\left[(n-\tfrac{1}{4})\pi\right]\left[1+0\left(\frac{1}{n}\right)\right],$$

therefore

$$_n\epsilon_m = (-)^m e^{(m-n-\frac{1}{4})\pi}\left[\cos\left(n\pi-\frac{\pi}{4}\right)+0\left(\frac{1}{m}\right)\right],$$

and

$$_m r_n = ({}_m x_n/b_n)^2 = \left(\frac{\alpha_m}{b_n}\right)^2\left(1+2\frac{{}_n\epsilon_m}{\alpha_m}\right)+0\left(e^{2(m-n-\frac{1}{4})\pi}/n^2\right).$$

Even when we are considering the node nearest to the clamped base, for which $m=n-1$, the expression

$$_m r_n = \left(\frac{\alpha_m}{b_n}\right)^2\left(1+2\frac{{}_n\epsilon_m}{\alpha_m}\right)$$

gives the nodal ratio with an error only of order

$$e^{-5\pi/2}/n^2 = 3\cdot 8820\times 10^{-4}/n^2.$$

This degree of accuracy is adequate to many applications which may arise. A higher degree of accuracy can, however, be obtained by working out a second approximation in the form

$$_m x_n = \alpha_m + {}_m e_n + {}_m \eta_n.$$

Other Conditions of Support.

It is worth while to enquire how far the characteristics of the serial arrangement of nodes in the higher tones is dependent upon the particular conditions of support at the base which we have selected for consideration. We propose now to consider the case of a conical rod in which the tip is, as before, free, but in which the conditions at the base are not specified.

The condition that the tip of the rod is free determines that in the equation for the displacement,

$$y = \mathrm{A J}_2 (2\sqrt{z})/z + \mathrm{B Y}_2 (2\sqrt{z})/z + \mathrm{C I}_2 (2\sqrt{z})/z + \mathrm{D K}_2 (2\sqrt{z})/z,$$

the constants B and D must vanish, so that the expression for y is of the form

$$y = \mathrm{A J}_2 (2\sqrt{z})/z + \mathrm{C I}_2 (2\sqrt{z})/z.$$

The nodal equation will be

$$\mathrm{A J}_2 (2\sqrt{z}) + \mathrm{C I}_2 (2\sqrt{z}) = 0,$$

and this equation may be written

$$\mathrm{J}_2 (x)/\mathrm{I}_2 (x) = -\mathrm{C}/\mathrm{A}, \tag{13}$$

where C/A is some constant depending upon the conditions at the base. Evidently there will be some characteristic constant—which we may write $a(n)$—associated with each tone. From our discussion of the nodal equation in the case when the base of the rod is clamped, namely,

$$\mathrm{J}_2 (x)/\mathrm{I}_2 (x) = \mathrm{J}_2 (b_n)/\mathrm{I}_2 (b_n),$$

it is evident that the roots of the nodal equation (13) will be arranged in pairs within successive pairs of the roots of the equation

$$\mathrm{J}_2 (x) = 0.$$

Further, if

$$\mathrm{J}_2 (x)/\mathrm{I}_2 (x) = a(n)$$

be the nodal equation for the nth tone, since it must have n roots, it is evident that we must have

$$a(n) = \mathrm{J}_2 ({}_n x_n)/\mathrm{I}_2 ({}_n x_n)$$

where $_n x_n$ lies between $(n - \frac{1}{4})\pi$ and $(n + \frac{1}{4})\pi$. We can, therefore, estimate the order of magnitude of $a(n)$, and as before we find that we get the nodes in the neighbourhood of the tip to a high degree of accuracy by putting

$$_m x_n = \alpha_m.$$

It is obvious that the nth root of the period equation, which we may denote by c_n, must be such as to make

$$_m c_n / c_n \leq 1, \qquad (_m c_n + 2\pi)/c_n > 1,$$

for otherwise there would be $(n+1)$ nodal ratios associated with the n tone. But as the nth root of an equation of the type

$$J_2(x) / I_2(x) = a,$$

lies whatever a may be, between $(n - \tfrac{1}{4})\pi$ and $(n + \tfrac{1}{4})\pi$, therefore

$$(n + 3\tfrac{3}{4})\pi > c_n \geq (n - \tfrac{1}{4})\pi.$$

Now, b_n, the nth root of the period equation in the case when the base of the rod is clamped, was found to be given by

$$b_n = (n+1)\pi + 0\left(\frac{1}{n}\right).$$

Therefore
$$c_n = b_n + 0\left(\frac{1}{n}\right) + \epsilon$$

where
$$-5\pi/4 < \epsilon < 11\pi/4.$$

Hence
$$(_m x_n / c_n)^2 = (_m x_n / b_n)^2 (b_n / c_n)^2 = (_m x_n / b_n)^2 \left(1 + 0\left(\frac{1}{b_n}\right)\right).$$

The nodal ratios in the neighbourhood of the tip are then evidently as before,

$$(\alpha_1 / b_n)^2, \qquad (\alpha_2 / b_n)^2, \qquad (\alpha_3 / b_n)^2 \ldots$$

if we neglect terms of order $1/n^3$. The intervals between consecutive nodes, in this neighbourhood, are clearly of order $1/n^2$.

Although we cannot specify the nodal positions in the other parts of the bar without some data as to the conditions of support at the base, we can see that the intervals between consecutive nodes, in the neighbourhood of the base, are of order $1/n$. Thus, as in the special case of the bar with a clamped base, the nodes crowd together with intervals of order $1/n^3$ near the tip, and becomes progressively further apart, the intervals being of order $1/n$ in the neighbourhood of the base.

Heat of Crystallisation of Quartz.

By Rames Chandra Ray, M.Sc.

1. *Introductory.*

Several attempts have been made to determine the heat of crystallisation of quartz, or the heat of transformation of quartz into vitreous silica, which is of importance in calculating the heat change involved in silicate reactions, and conflicting results have been obtained by different workers. Tschernobaeff[*] determined the heats of formation of certain silicates by Le Chatelier's method,[†] measuring the heat evolved when a mixture of the dry substances were made to react by combustion of a given weight of carbon in a bomb calorimeter. From the difference of heat of reaction of silica glass and calcium carbonate, and of that of sand and calcium carbonate, Tschernobaeff found that the heat of transformation of quartz into vitreous silica was very small, and equal to only 0·9 Kgrm.-cals. per grm.-molecule. But from the results published later by Tschernobaeff and Wologdine[‡] Dr. M. W. Travers has calculated the heat of transformation of silica and found it to be equal to 7·3 Kgrm.-cals.[§]

From the measurements of conductivity, Tammann[||] showed that amorphous and crystalline silica dissolved in hydrofluoric acid in one and the same state, so that the difference between the heats of solution of the two substances would represent the heat of transformation from the crystalline to the vitreous state. Cunningham[¶] was the first to use the hydrofluoric acid method for this purpose. His experiments, however, were more or less of a qualitative nature, but he stated that he obtained a distinct indication of a large difference between the heats of solution of crystalline and vitreous silica.

The difficulty of determination by this method lies in the fact that the reaction, especially in the case of quartz, is extremely slow. The same method was employed later by Mulert[**] and Wietzel[††] in order to determine

* 'Rev. de Métallurgie,' vol. 2, pp. 729–738 (1905).

† 'C. R.,' vol. 120, p. 623 (1895).

‡ 'C. R.,' vol. 154, p. 208 (1912).

§ 'Jour. Soc. Glass Tech.,' vol. 4, p. 220 (1920).

|| 'Kristallisieren und Schmelzen.'

¶ 'Proc. Roy. Dub. Soc.,' New Series, vol. 9, p. 412 (1901).

** 'Zeit. f. Anorg. Chem.,' vol. 75, p. 206 (1912).

†† *Ibid.*, vol. 116, p. 75 (1921).

the heat of crystallisation of silica.   Both of them obtained very nearly the same value for the difference between the molecular heats of solution of crystalline and vitreous silica, namely, 2·21 and 2·32 Kgrm.-cals. respectively. But it will be shown in this paper that these values are far too low and that the error is probably due to the fact that, in order to obviate the slowness of the reaction, both these workers subjected their samples to long grinding, which causes a considerable increase in the heat of solution in the case of the crystalline material.   In the case of Mulert's experiments, the quartz was ground in an agate mortar for 17 hours, and then the powder was subjected to a special washing process to separate the finest particles. Finally, he obtained about 1 grm. of substance from 1 kgrm. of the powdered quartz.   Rock crystal, which was used in Wietzel's experiments, was ground in a mechanically operated agate mortar for 100 hours.

2. *Method of Determination.   Analysis and Determination of Specific Heat of Aqueous Hydrofluoric Acid.*

Preliminary determinations of heats of solution were carried out with a thermometer coated with wax to prevent it from being attacked with hydrofluoric acid.   These gave the necessary experience, and showed that the difference between the molecular heats of solution of quartz and silica glass was approximately equal to 7 calories.   Silver sand was used for crystalline silica, and it was found that particles which passed through a 20-mesh sieve were quite suitable for the reaction.   In the case of silica glass, however, particles which passed through a 40-mesh sieve had to be used; for, if finer particles were used, the reaction proceeded too rapidly to follow the rise of temperature easily.   It was found that this difference in the size of the particles did not appreciably affect the heats of solution, for silica glass which was passed through a 20-mesh sieve gave almost the same heat of solution as that passed through a 40-mesh sieve.

The final determinations were carried out with a thermometer divided into tenths of a degree.   The bulb of the thermometer was protected with a platinum cap which was especially constructed to fit the bulb of thermo-meter closely.   A small quantity of mercury was introduced into the cap to obtain an intimate contact between it and the bulb of the thermometer. The top of the cap was attached to the stem of the thermometer with a small piece of rubber tubing.   The calorimeter vessel was a platinum crucible of about 60 c.c. capacity, which fitted tightly into the bottom of a fairly long Dewar's vessel, the mouth of which was closed with cotton-wool during the experiment.   The thermometer itself was used as the stirrer.

The silver sand used in the determinations was first freed from finer

particles by sieving, and those particles which passed through a 20-mesh sieve were purified by boiling repeatedly with hydrochloric acid, then washing with distilled water and drying at 150° C. The silica glass, obtained from the British Thermal Syndicate, was broken into small pieces by a hammer, and then crushed in an agate mortar. The particles which passed through a 40-mesh sieve were boiled with hydrochloric acid, washed, and dried in the same way as the sand.

The hydrofluoric acid used was found to possess approximately a specific gravity of 1·17 at the ordinary temperature. The acid was analysed in the following manner :—

A weighed quantity of the acid in a platinum dish was diluted with water, and an excess of sodium carbonate was added. A large quantity of ammonium carbonate was then added, and the solution was heated. After standing for 12 hours, the precipitated silicic acid was filtered. The filtrate was treated with a small quantity of ammoniacal zinc oxide solution, boiled until the ammonia was completely expelled, and the precipitate of zinc silicate and oxide was filtered and washed with water. The precipitate was treated with hydrochloric acid, and the silicate, obtained by evaporation on the water bath in the usual way, was added to the silica obtained in the first operation. The filtrate, after treatment of the ammoniacal zinc oxide, was treated with an excess of calcium chloride solution, filtered and washed with hot water. The precipitate was dried and ignited in a platinum crucible. After cooling it was carefully treated with an excess of acetic acid and evaporated to dryness on a water bath. The dried mass was taken up with water, filtered, washed free from calcium acetate, dried and ignited. The following results were obtained :—

No. of experiment.	Percentage of SiO₂.	Percentage of H.F.
I	0·89	34·59
II	0·86	34·64
Mean	0·88	34·62

The specific heat of the hydrofluoric acid was measured by a slight modification of the method described by Müller-Pfaundler.* The same current of electricity was passed through the same resistance of fine platinum-iridium wire for the same time into weighed quantities of the aqueous hydrofluoric acid and water placed in the same vessel. The initial temperature of the liquids was as much below the ordinary temperature as the

* 'Lehrbuch der Physik,' 8th ed., vol. 2, p. 2311.

final temperature was above it, so that the loss of heat during the experiment which lasted from 8 to 10 minutes, and the alteration of the resistance of the wire by temperature, were practically eliminated. If m be the weight of hydrofluoric acid, c its specific heat, t^0 the rise of temperature, and m^1 the weight of water, c^1 the specific heat of water, t^1 the rise of temperature, then $mc + w/m^1\ c^1 + w = t^1/t$, where w is the water equivalent of the calorimeter. The following values were obtained for the specific heat of different strengths of hydrofluoric acid :—

<div align="center">Table I.</div>

Percentage of HF (by weight) in solution.	Specific heat.
10	0·908
20	0·838
30	0·756
34·6	0·724

3. *Determinations of the Heats of Solutions of Quartz and Silica Glass.*

In order to determine the heat of solution, a definite quantity of hydrofluoric acid (29·40 grm.) was introduced into the calorimeter, and stirred by means of the thermometer as already described, and the temperature noted at intervals of 1 minute. After 3 to 5 minutes a weighed quantity of the purified and dried silver sand, or silica glass, was quickly poured into the calorimeter and the rise of temperature was noted after every minute with constant stirring. The action was allowed to continue from 15 to 25 minutes, and was then stopped by adding a large quantity of cold water. The quantity of material used in different experiments varied between 3 and 8 grm. In the case of the silver sand, 0·3 to 0·6 grm. of the substance dissolved and the rise of temperature was never less than 6° C.; whilst in the case of the silica glass as much as 1·4 grm. of the substance dissolved and the rise of temperature was as high as 34° C. After the reaction had been stopped, the contents of the calorimeter was washed out, and the undissolved silver sand, or silica glass, as the case might be, was filtered off, washed with water, and weighed. From the loss of weight, the amount of silica dissolved could be determined. In two cases, the amount of silica in solution was estimated directly, and the amounts dissolved were found to be the same as those calculated from the weight of the undissolved silica, showing that no loss of silica took place, during the reaction, as silicon tetrafluoride.

Mulert (*loc. cit.*) has shown that when silica is treated with aqueous hydrofluoric acid only hydrofluorsilicic acid is formed, six molecules of the acid taking part in the reaction for each molecule of silicon dioxide. The loss of heat on account of radiation was determined separately for each experiment, by determining the rate of cooling of water with the same amount of sand or silica glass. Knowing the loss of heat in the case of water, the loss in the case of hydrofluoric acid could be calculated; for the quantities of heat given off in the same time would depend on the weights of the liquids and their specific heats. The following table gives the details of experiments and the results obtained :—

Table II.

Substance.	Size of particles.	Weight of substance added in grms.	Weight of substance dissolved in grms.	Time of reaction in mins.	Rise of temperature.	Water equivalent of calorimeter.	Heat of solution per grm.-mol. in Kgrm.-calories.
Silica glass ...	40-mesh	6·4090	1·1550	14	28·80	4·67	37·33
,, ,, ...	,,	6·7048	1·0744	13	25·32	4·67	37·04
,, ,, ...	,,	5·2174	1·3620	16	32·98	4·67	37·27
,, ,, ...	,,	3·3098	0·5566	11	13·29	4·67	37·36
,, ,, ...	20-mesh	4·7622	1·4689	7	34·40	4·67	37·22
Silver sand ...	,,	8·0914	0·6044	22·5	11·30	4·67	30·32
,, ,, ...	,,	7·7712	0·6016	25	11·23	4·67	30·18
,, ,, ...	,,	5·2337	0·8668	16	7·01	4·67	30·38
,, ,, ...	,,	4·0620	0·3127	13	6·02	4·67	30·29
,, ,, ...	,,	3·8740	0·4938	20	9·50	4·67	30·30

The mean of the values of the heats of solution of silica glass in hydrofluoric acid is 37·24 Kgrm.-cals. per grm.-molecule of silicon dioxide, and that for silver sand is 30·29 Kgrm.-cals. per grm.-molecule. The difference between the two heats of solution is 6·95 Kgrm.-cals. Therefore the heat of crystallisation of quartz at the air temperature may be represented thus :—

$$SiO_2 \text{ (vitreous)} = SiO_2 \text{ (quartz-cryst.)} + 6\text{·}95 \text{ Kgrm.-cals.}$$
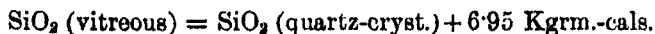
This value is of the same order of magnitude as that calculated from Tschernobaeff and Wologdine's results, and is much higher than those obtained by Mulert and Wietzel.

4. *Change in the Heat of Solution of Quartz and Silica Glass ground for a long time.*

In taking up this investigation, it was anticipated that the low value of the heat of transformation of silica obtained by Mulert and Wietzel

(*loc. cit.*) would be found to be connected with the fact that they submitted the crystalline material to prolonged grinding.   Sir George Beilby has shown that grinding of crystalline substances to powder does not simply consist in their reduction to finer and finer crystalline fragments, but it involves .the transformation of, at any rate, a part of the substance into the vitreous condition.*   Hence it was considered worth while to study the effect of long grinding on silver sand as well as silica glass.

The silver sand and silica glass which were used in the above experiments were separately ground, for 15 hours each, in a mechanically operated agate mortar.   The powders thus obtained were very fine, and passed completely through a 200-mesh sieve.   They were again dried at 150° C., and the heats of solution were determined in the usual way.   As the finely powdered substances dissolved readily it was not necessary to add the material in excess as in the case of the experiments described above.   In the following experiments the substance added was entirely dissolved.   The following are the results of the experiments :—

Table III.

Substance (ground for 15 hours).	Amount added in grms.	Rise of temperature.	Water equivalent of calorimeter.	Time of reaction in mins.	Heat of solution per grm.-mol. in Kgrm.-calories.	Mean.
Silica glass	0 ·7004	16 ·01	4 ·67	7	36 ·93	} 36 ·95
,, ,, ...	0 ·4786	11 ·50	4 ·67	5	36 ·96	
Silver sand	0 ·8080	17 ·09	4 ·67	12	32 ·47	} 32 ·46
,, ,, ...	0 ·4526	9 ·62	4 ·67	9	32 ·45	

It will be noticed that grinding has a considerable influence on the heats of solution in the case of the quartz.   The molecular heat of solution of silver sand which was ground for 15 hours was found to be 2·17 Kgrm.-cals. higher than the one which was not subjected to grinding.   Using a 35-per-cent. hydrofluoric acid solution Wietzel (*loc. cit.*) found 33·65 cals. as the heat of solution of rock crystal which had been ground for 100 hours.   It is evident that the action of grinding modifies the crystalline material, and partially converts it into the vitreous form.   It s clear from the results of the experiment that the increased heat of solution of the ground substance is not due to the increased heat of hydration on account of the fineness of the particles.   The slight lowering of the heat of solution of

* 'Aggregation and Flow of Solids,' p. 119 (1921).

silica glass on grinding, however, is not easily explained. All the samples used for the experiments were very kindly examined by Mr. H. Mitter, M.Sc., who is working in Prof. Bragg's laboratory, by the X-ray method, and he could not find crystalline material in any of the samples of silica glass. This is in accordance with the results obtained by Kyropoulos,[*] who examined finely powdered silica glass.

5. *Heat of Crystallisation of Quartz at Higher Temperatures.*

The latent heat of crystallisation of quartz at higher temperatures can be calculated by means of the expression

$$(\text{Ccr} - \text{Cgl})\, t = \text{Lo} - \text{Lt},$$

where Ccr and Cgl are the mean interval molecular heats of the crystalline and glassy materials, and Lo and Lt are the molar latent heats at $0°$ and $t°$ respectively. The values of Ccr and Cgl can be obtained from the mean interval specific heats, which have been determined by White[†] for intervals between $0°$ and temperatures up to $900°$ C. It was found that, contrary to the usual experience, the value of Cgl is less than that of Ccr over the range of temperature investigated, the difference between the values attaining a maximum at about $700°$, then diminishing and having a tendency to coincide near the melting-point. The mean interval molecular heats in Kilogram-calories per gram-molecule at $900°$ are :—

Quartz .... 0·015576

Silica glass .... 0·015072

so that $\qquad (\text{Ccr} - \text{Cgl}) \times 900 = 0·45$

and $\qquad\qquad\qquad \text{L900} = 6·50.$

At higher temperatures the difference would continue to diminish, and at $1300–1400°$ the value of Lt would probably not be far from the value at the air temperature. Finally, it may be mentioned that Washburn[‡] calculated the latent heat of fusion of crystobalite from the difference between the melting-point of crystobalite and the silica-alumina eutectic point and obtained the value 6·80 Kgrm.-cals. per molecule. This would also be approximately equal to the heat of crystallisation of quartz at the melting-point ($1610°$). Since the latent heat of the change,

$$\text{SiO}_2 \,(\text{quartz}) \rightleftharpoons \text{SiO}_2 \,(\text{crystobalite})$$
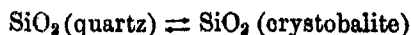
is probably very small, one would expect a close agreement between Washburn's value and that arrived at in the case of quartz.

[*] 'Zeit. f. Anorg. Chem.,' vol. 99, p. 198 (1917).
[†] 'Amer. J. Sci.,' vol. 47, p. 1 (1919).
[‡] 'Jour. Amer. Cer. Soc.,' vol. 2, p. 1008 (1919).

6. *Summary.*

(1) The specific heats of aqueous hydrofluoric acid of different concentrations have been determined and the results recorded in Table I.

(2) The heats of solution of quartz and silica glass in aqueous hydrofluoric acid have been determined (Table II), and the difference, which represents the heat of crystallisation of quartz at the ordinary temperature, is found to be equal to 6·95 Kgrm.-cals.

(3) From determinations of the heats of solution (Table III) it has been shown that grinding affects the crystalline material, which is partially converted into the vitreous state.

(4) The latent heat of crystallisation of quartz has been calculated at higher temperatures, and it is shown that near the melting-point the heat of crystallisation of quartz is very nearly equal to that at the air temperature.

The Properties and Molecular Structure of Thin Films.
Part III.—*Expanded Films.*

By N. K. ADAM, M.A., University of Sheffield.

1. *Expansion of Films of the Fatty Acids on Dilute HCl.*

In the previous paper an account was given of the properties of the films over a range of temperature low enough for it to be permissible to regard the molecules as in direct contact over the whole area, except perhaps for a very slight tendency to separate under the lowest compressions; this tendency being perhaps analogous to vapour pressure. The films in this condensed condition were either solid or liquid. Within the accuracy of my experiments, the mechanical properties of condensed films were independent of temperature.

The present paper describes the phenomena observed above this range of temperature. At a certain temperature all the films expand along the surface, the actual temperature of expansion depending both on the nature of the substance in the film, and on the composition of the solution. The phenomena exhibited by films of the fatty acids on dilute HCl have been the most thoroughly investigated, and will be first described.

Fig. 1 gives the compression curves of myristic acid (C$_{14}$) at various temperatures, 3·5°, 6°, 7·3°, 8°, 14°, 20°, 28°, and 32·5°. Those at 3·5° and 28°

Fig. 1.
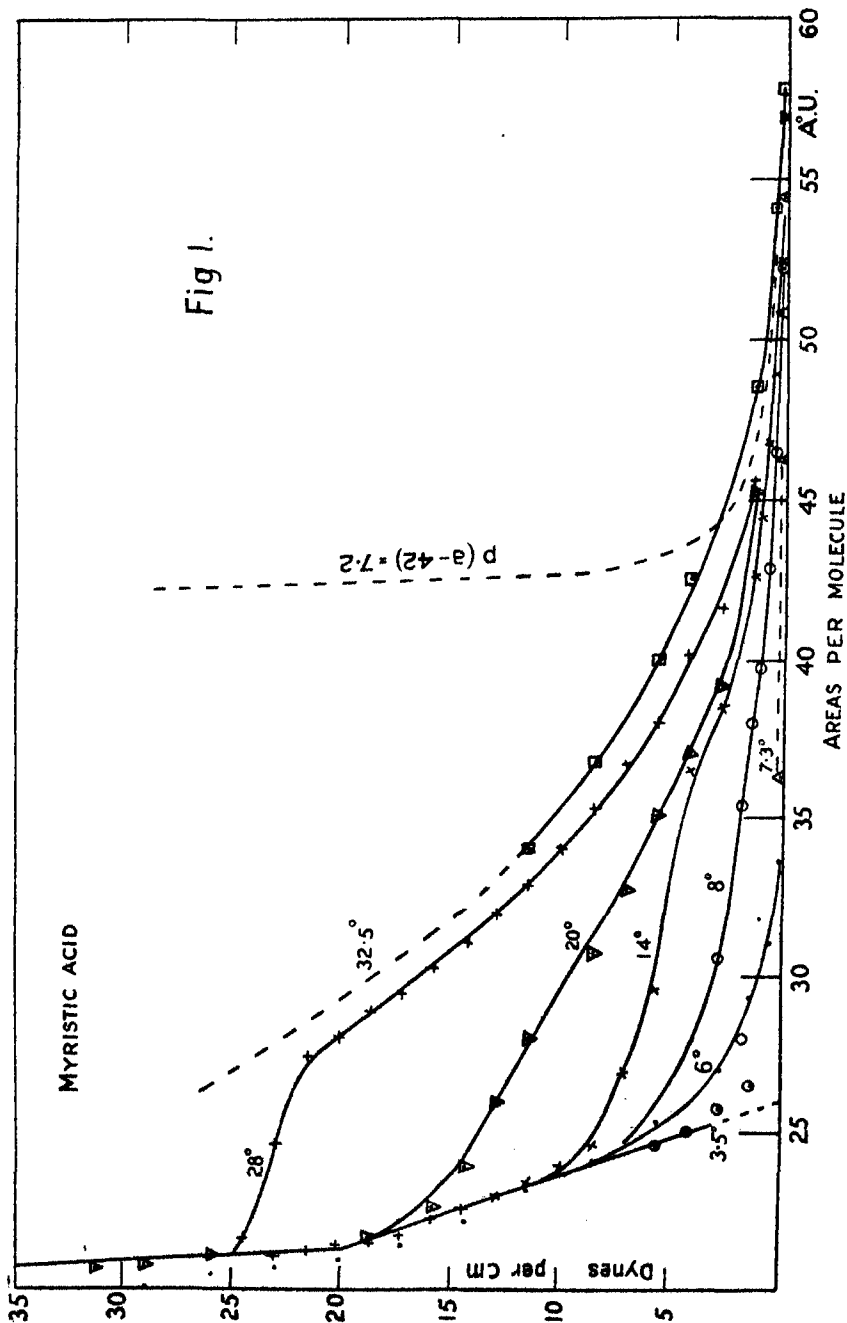
were done on N/10 HCl, the remainder on N/100.   There appeared to be a slightly greater extension of the films on the N/100 than on the N/10, for a few degrees below 10°, but the difference was almost within the experimental error.   The temperatures are probably correct to 0·5°.   The curve at 3·5° is practically the same as the typical curve of compression of condensed films of fatty acids on this solution (Part II, fig. 2, III).   At 6° a slight extension appears, below 10 dynes per centimetre compression, but at 35 Å.U. area the "vapour pressure," referred to in the last paragraph of Part II, was still below 0·29 dynes per centimetre.   At 7·3°, in one experiment, the "vapour pressure" was found to be almost exactly 0·29 dynes per centimetre ; it was possible to alter the area over the range indicated by the dotted line with scarcely any movement of the balance float.   At 8° the "vapour pressure" was nearly five times as great.   At 14° and higher temperatures, the lowest portion of the curves somewhat resembles a hyperbola, but at a fairly definite point the curves become of less steep slope and pass rapidly to the left (the area of the film decreasing), rising steeply again only when nearing the typical condensed curve.   There are thus two points of inflexion in the curves, the second being on a part of fairly gentle slope.   Many experiments have been done at intermediate temperatures, which showed that the compression required to reach this second point of inflexion rises steadily with increasing temperature, curves being distinguishable by this ordinate when only about 1° C. apart. These curves occupy positions intermediate between those shown in the figure. Finally, when the temperature rises more than about 25° above that at which the first divergence from the condensed curve is perceptible, the inflexions are no longer visible on the curves, since the compressions which would be required to reach them are so great that collapse of the films has already occurred.

No appreciable hysteresis has been observed in any experiment upon expanded films.

All the fatty acids mentioned in Part II have been examined on dilute HCl, except cerotic, and all show substantially the same phenomena, though at different temperatures.   In the cases of oleic, lauric, and tridecylic acids, only the more or less hyperbolic part of the curves could be traced experimentally, because the whole or the main part of the transitional range of temperature was below 0° C.   Erucic and elaidic acids also gave films not completely condensed at the lowest temperatures which could be reached, though a large part of the transitional region was examined.

In fig. 2 the area of the film is plotted against the temperature under a small compression of 1·4 dynes per centimetre, for palmitic acid.   There is only a small transition range of temperature between the upper slightly

sloped line of the expanded film, and the lower horizontal line of the condensed film, the change being completed in about 13° C. The points from which the line has been drawn were determined on N/100 HCl; a few ringed points obtained on N/10 acid are added, which indicate that the expansion is, if anything, more sudden on this solution, but occurs at the same mean temperature. Similar curves have been obtained for all the fatty acids on this solution, except where the temperature of expansion was below 5°. All have the same S shape, the interval of temperature not being greater in any case than for palmitic acid.

Areas at 1·4 dynes compression.
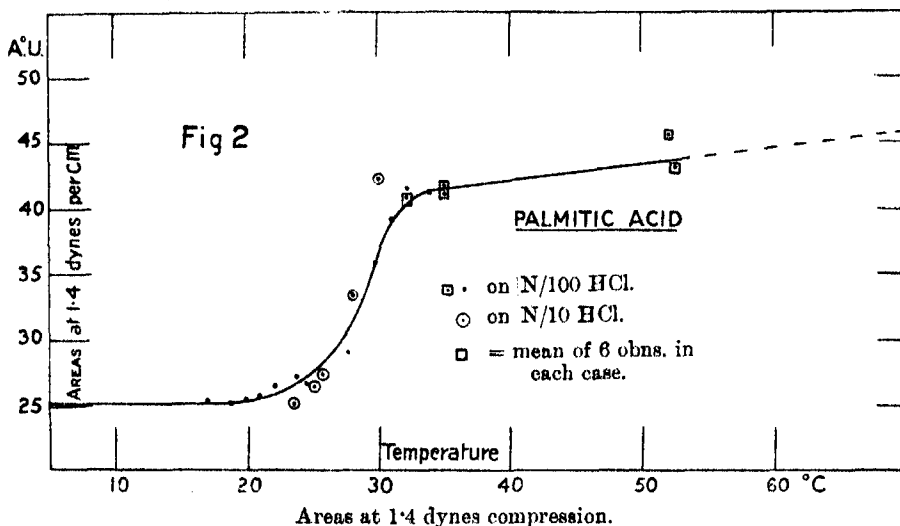
The coefficient of thermal expansion of the expanded films would, from the analogy with a gas to be developed later, be expected to be the same as that of a perfect gas. Unfortunately, the difficulties of experiment are too great to make a satisfactory measurement of this quantity. In fig. 2, the upper line has been drawn with a slope which corresponds to this coefficient of thermal expansion. The points in rectangles have been determined with the greatest care, but they do no more than confirm the order of magnitude of this slope. Above about 50° accurate measurements with palmitic acid become impossible on account of solubility. Neither has it been found possible to carry accurate measurements of the expanded areas of other substances to temperatures sufficiently above the expansion temperature to give a better verification of the coefficient of increase of the expanded area with temperature. Referring to fig. 1, an indication is given that there is some lateral shifting of the hyperbolic part of the curves as a whole to the right as the temperature rises (although probably a part of the difference between the positions of the curves

at 28° and 32·5° is fortuitous); and I have obtained similar results on other films also where sufficiently accurate experiments have been done. This effect of temperature on the expanded films is therefore existent at all compressions, although the data are not accurate enough to give a measure of its amount.

The influence of the length of the hydrocarbon chains in the series of saturated acids on the temperatures of expansion was most interesting, a steady rise being observed with increasing molecular weight. The data are collected in Table I. It will be noticed that there is no difference between the even and odd members of the series, such as is well known in the melting points of the crystals.

A slight difference in the areas to which expansion takes place also exists between acids of different length of chain, and is very probably due to the attraction between the chains being greater in the long chains than the short, so that there is a greater correction to be subtracted from the area, analogous to the a/v^2 correction in Van der Waals' equation.

The unsaturated acids expand at lower temperatures than the saturated acid with the same number of carbon atoms. The effect of a double bond in the $\alpha\beta$ position on this property is much the same as that of shortening the chain by two carbon atoms. For double bonds in the middle of the chain the stereochemical configuration is very important, the form with the lower melting point (oleic and erucic) expanding some 70° lower than the corresponding saturated acid, while the other isomer expands only about 40°–45° lower. These differences are probably a consequence of different lateral attraction of the chains, a cause which may also be responsible for the slight differences in the areas to which the films of these substances expand.

The data in Table I were determined at the arbitrary small compression of 1·4 dynes per centimetre, which is the lowest compression at which accurate measures of area have been obtained. The temperature of half-expansion is the temperature at which the area of the film was the arithmetic mean between the areas of the completely expanded film and of the condensed film. This temperature is better defined, owing to the shape of the curve, than the temperature of commencement or of completion of expansion. The areas for the saturated acids have been determined with the greatest care, in order to establish whether the expanded area really varied with molecular weight in this series or not; probably, except for the acids with the two longest chains, the error is well within one unit. Each of the figures in the fourth column up to C_{21} is the mean of six good measurements. The areas given have been determined at temperatures not more than 10° above that at which expansion becomes complete under 1·4 dynes, in order to minimise errors due to

solubility of the molecules; but control experiments giving closely agreeing results were done in most cases at higher temperatures, in order to make sure that the area measured was really that of a fully expanded film.

In order to compare the areas for different members of the series, they have been corrected to 0°, using the coefficient of thermal expansion of a gas. Of course, at this temperature most of the films are not, in fact, expanded. Sufficient measurements have, however, been made at the same temperature on members of the series differing by up to three carbon atoms, to make sure that the gradual decrease in area occupied with increasing molecular weight is not due to the correction being erroneous.

Table I.—Expansion of Films of Fatty Acids on dilute HCl, under 1·4 dynes per cm. compression.

Acid.	No. of carbon atoms.	Temperature of half expansion.	Area of expanded film.	Temperature of determination of area.	Area corrected to 0° C. (mean).
		°		°	
Lauric	12	below 0	48·2 47	16·5 14	45·1
Tridecylic	13	below 0	45·6 43·6	15·5 11·5	42·5
Myristic	14	9	43·5 43·9	18 24	40·6
Pentadecylic	15	19·5	42·0 42·2	25·3 22·5	38·8
Palmitic	16	28·5	41·3 41·7	35 34·5	36·8
Margaric	17	37·5	42·6 41·7	41 43·5	36·6
Stearic	18	46	42·9 43·2	52·5 53	36·1
Heneicosoic	21	65·5	(46·0) (47·5)	77 80	(36·4)
Behenic	22	72·5	(45·9)	75	(36·0)
Iso-oleic	18	25	(46)	35	(40·8)
Oleic	18	below 0	(52·5)	10	(50·5)
Elaidic	18	− 0·5*	(47)	10	(45·4)
Erucic	22	4·5	(47)	10	(45·4)
Brassidic	22	34	(45)	40	(39·2)

Figures in brackets are less accurate than the others, but are probably within two units of the correct value.

* For elaidic acid the point of half expansion is not directly observable; but comparison of the curves similar to those in fig. 1, obtained for erucic and elaidic acid, showed that corresponding stages of expansion are reached 5° lower with elaidic than with erucic acid.

2. *Expansion of Fatty Acids on other Solutions.*

Some of the acids have been examined upon distilled water, on a phosphate solution of $P_H 6$, and on N/10 soda. These results have not been obtained as accurately as the preceding, but they show several points of interest.

On distilled water, and on the P$_H$6 solution, the temperatures of expansion were not quite definite, but depended on the time the solution had been in the trough, this effect being no doubt connected with the other effects of the age of the solution described in Part II. The temperatures varied from about 5° to 15° higher than the expansion temperatures for the same acids on HCl. The lowest temperatures were obtained on the fresh solution, the highest after standing some time in the trough. The areas to which expansion extended were very slightly less than on HCl.

On N/10 NaOH solution the measurements of area were probably slightly smaller than the true values, as there was some solution; but this was surprisingly slow with acids higher than palmitic. The expansion was the largest yet found, being to about 120 Å.U. at 1·4 dynes per centimetre. The temperatures of expansion were about 30° lower than on N/100 HCl.

On all these solutions the effect of increasing the length of the chain by one carbon atom was to raise the temperature of expansion by exactly the same amount as on HCl, *i.e.*, about 10° in the region of 0°, and about 8·5° near 40°.

3. *Expansion Phenomena with other Substances.*

The curves of compression for ethyl palmitate at three temperatures are given in fig. 3, and also the variation of area under 1·4 dynes per centimetre

Fig 3
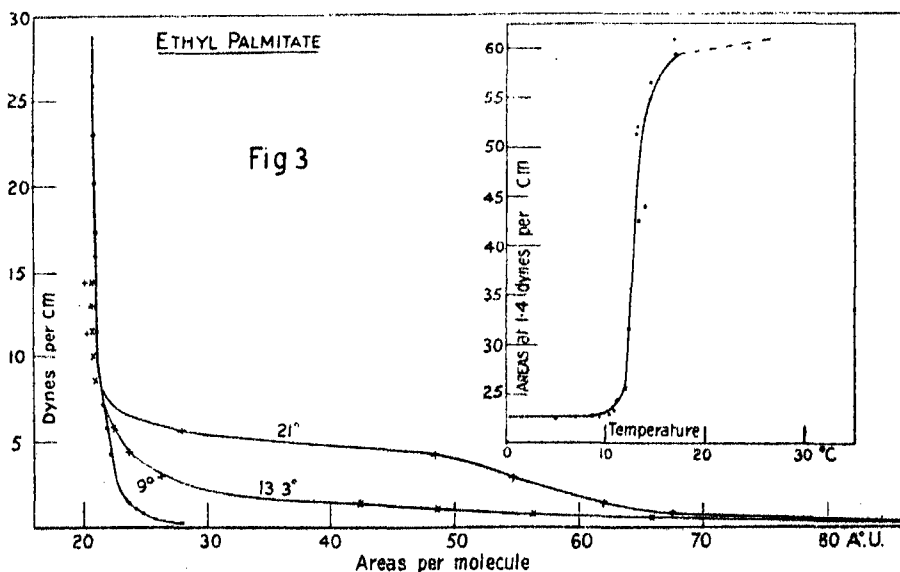
compression with temperature. The expansion is to greater areas than with the acids on neutral and acid solutions, and the curves at temperatures in the transition region are flatter, but the main points of figs. 1 and 2 are

reproduced. The behaviour of ethyl palmitate was exactly the same in respect of temperature of expansion and area on HCl as on water. Very similar expanded curves were obtained on methyl, propyl, butyl and octyl palmitates. Methyl palmitate requires a higher temperature for expansion than ethyl; propyl and the esters of higher alcohols up to octyl, however, are more easily expanded, and condensed films of these substances probably only exist below 0°. There is an interval between the temperature of expansion of ethyl palmitate and ethyl stearate almost equal to that between the expansion temperatures of the two fatty acids, whose chains differ in length by two carbon atoms, and whose temperatures of expansion lie in the same region.

Tripalmitin and tristearin on distilled water expand at temperatures which differ by considerably less than the usual difference between films of substances whose chains differ in length by two carbon atoms. This is the only exception yet found to the rule that adding one carbon atom to the chain raises the temperature of expansion by the same amount, whatever the nature of the head or the length of the chain; and this anomaly is no doubt connected with the fact that the films of these substances break up on expansion, not into single chains, but into groups of three. Table II gives the collected results.

Table II.—Expansion of various Substances on Distilled Water, under 1·4 dynes per cm. compression.

Substance.	No. of carbon atoms in hydro- carbon chain.	Temperature of half expansion.	Area of expanded film corrected to 0° C.
		°	
Methyl palmitate	16	27·5	(46)*
Ethyl ,, ...	16	18	55
Propyl ,, ...	16	(below 5)	(76)
n-Butyl ,, ...	16	(below 5)	(74)
n-Octyl ,, ...	16	(below 5)	(76)
Ethyl stearate	18	33	45·4
Tripalmitin	16	48	29·5
Tristearin	18	57	29·9
Cetyl alcohol..........................	16	49	(30·8)†
Heptadecyl urea	17	55	33
Octadecyl urea	18	62·5	33·7
Stearic amide..........................	18	58	32·2
Stearic nitrile	17	26	36·4
Octadecylamine hydrochloride	18	(26·5)	46

   * Methyl palmitate dissolved at the temperature of this measurement fast enough to cause slight uncertainty.

   † Also rendered probably too small by solution.

4. *Comparison between the Expanded Films and Gases.*

The only theory of the expanded state which seems at all probable is that, in the process of expansion, the molecules become separated from each other and move about independently on the surface. In this condition the film resembles a gas, and, since the molecules are confined to the surface by reason of their insolubility, the barriers on the surface take the place of the walls of the vessel confining the gas. The pressure on the barriers thus differs in the case of the expanded films from the pressure exerted by the condensed films, in being exerted by a series of impacts rather than by a steady thrust. There is therefore on the surface, in the expanded films, a considerable space not actually covered by the molecules, at any instant.

The very close resemblance between the "isothermals" in figs. 1 and 3 and the isothermals of a vapour near the critical point is obvious, and is strong evidence in support of this way of regarding the films. The fully expanded films are not rectangular hyperbolas; however their departure from this form is not evidence against the view that the films are analogous to gases, but is a measure of the corrections to the simple gas laws which must be applied to the films, for the area occupied on the surface by the molecules, and for their mutual lateral attractions. That these corrections will need to be rather larger than in the case of gases is natural, since the difference in area between the condensed and the expanded films is much less than the difference between the volumes of most substances in the liquid and vapour states.

There is, however, an important point of difference from a gas. In a gas the molecules which exert the pressure are the only ones in the enclosure, and the only collisions they experience are those with the walls and with other molecules, which will later themselves strike the boundaries and exert pressure. The film molecules, however, are continually subject to forces from the molecules of the underlying solution, both attractions and repulsions; and these underlying molecules do not themselves at any time exert tangential forces on the boundaries. It is these forces which probably mainly determine the motions of the film molecules. The intensity of these forces from the molecules of water and substances dissolved therein will depend upon the composition of the solution and upon the chemical nature of the heads of the film molecules; it will also increase with the temperature. A fuller understanding of the properties of the expanded films should therefore be of service in shedding light on the problem of the nature of the forces between solvent and dissolved molecules.

5. Nature of the Process of Disruption of Condensed Films, or " Vaporisation."

The attractive forces which hold the condensed films together had to be considered even in the discussion of condensed films. It was stated at the beginning of Part II that the theory would be developed on the assumption that there was no tangential surface force on the films *as a whole* from the water molecules. When, however, the individual molecules of a condensed film are considered, the random tangential movements of the molecules of water (and substances dissolved in it) must impart similar movements to the film molecules; the resultant of which, since the motions are equally distributed in all directions, must vanish when an area large enough is considered. Such forces will tend to separate the film molecules from one another and to cause expansion when they reach sufficient intensity to overcome the forces of lateral adhesion between the film molecules. The legitimacy of neglecting the tangential forces and motions when a large area is considered is evident; in the precisely similar case of Brownian movement, the particles show no movement if large enough, because the number of collisions with moving molecules is so great that their resultant in any direction practically vanishes, while the smaller particles receiving fewer impacts are able to discriminate between the random motions of the molecules.

The influence of the contribution made to the lateral attractions by the hydrocarbon chains is obvious when the expansion temperatures of successive members of the homologous series are considered. The addition of one CH_2 group to the molecule makes a definite rise in the expansion temperature of the film.

It is most probable, however, that the polar heads of the molecules also contribute considerably towards the lateral cohesion. In the preceding paper it has been shown that the heads of the molecules are an important factor in the solidity or otherwise of the films, so that cohesive forces are to be presumed between them. Also the same polar groups must have a considerable attraction for one another in short chain compounds, since these possess considerable cohesion. It is difficult, however, at present to decide what proportion of the lateral attraction must be ascribed to the heads and what to the chains.

6. Corrections to the Expanded Films for the Area Occupied by the Molecules and the Lateral Attraction.

For a perfect gaseous film the equation of the isothermals would be $pA = KT$, A being the area and p the compression in dynes per centimetre

This equation does not fit the curve in fig. 1 at 32·6°, and in order to obtain the right correction it will be necessary to carry the calculations of the correction required from the area occupied by the molecules to much greater accuracy than is done in Van der Waals' equation. By repeating the calculations in Jeans' 'Dynamical Theory of Gases,' 1921 edition, pp. 126–127, substituting areas for volumes, it is easily seen that the correction to be subtracted from the area of the films, corresponding to Van der Waals' "b," is here twice the area of the molecules, instead of four times as in the case of gases. The total area of a film composed of closely packed chains has been found to be 21·0 Å.U. per molecule; the dotted curve in fig. 1 is that of $p(A-42)=7·2$, but the actual curves pass very much to the left of this. It is well known, however, that the "b" correction to gases is too large at high condensations, so this lack of agreement is not evidence against the more or less independent motion of the molecules in the expanded films and their analogy with gases. It should be pointed out also that although the total area occupied by a film of close packed chains or heads is known, the manner of packing is not, nor whether the collisions in the expanded state take place between the heads or the chains. There is, therefore, some uncertainty as to the area of a single molecule which should be taken into account in considering the correction just discussed.

It does not seem worth while to attempt a quantitative correction for the lateral attractions until the large correction for the area covered by the molecules has been carried to much greater accuracy. An effect which is probably due to this attraction, namely, that the molecules with longer chains expand to somewhat smaller areas, has already been mentioned.

7. *Difficulties attending any Conceptions of the Expanded Films other than the Analogy with Gases.*

On the explanation given there are spaces not covered by the molecules. The expanded films are therefore " one molecule thick," though not in quite the same sense as the condensed films. It does not seem possible to account for the phenomena on any explanation in which the molecules are assumed touching all over the area.

The increase of area cannot be due to the molecules lying flat on the surface. The area even at very low compressions is often not more than 50 Å.U. Since the cross-section of a molecule of stearic acid is 21·0 Å.U., assuming a circular cross-section, its diameter must be 5·2 Å.U., and therefore the minimum area it could occupy when lying flat would be 109 Å.U., which is much too large. Moreover, if the expanded state were due to some only of

the molecules lying flat, the area per molecule would probably increase with the length of the chain; whereas experiment shows, on the contrary, that the area is somewhat less for long molecules than for short.

It might also be suggested that the molecules are vertical and in contact everywhere in the film, but are subject at higher temperatures to such violent thermal oscillations that they require a larger area. It would be exceedingly difficult to explain the sudden nature of the expansion on this hypothesis; a steady increase in area with rising temperature would rather be expected, instead of the rapid rise in figs. 2 and 3. To explain the discontinuity the process must be analogous to a transition from one form to another, or change of state; and the only common change of state in other states of matter which is attended with large change in volume is that from liquid or solid to gas. Therefore, the surface change of state which causes the expansion of the films must be analogous to the vaporisation of a condensed substance.

Finally on any theory of the expanded films which could come in this class, it would be necessary to give an explanation of the striking resemblance between the "isothermals" of the films and those of a vapour near the critical point. The oscillations in the chains would have to be of a very extraordinary kind for their amplitudes to be diminished by increasing compression in the manner required to fit these curves.

8. *The Orientation of the Separated Molecules in the Expanded Films.*

Exact information as to the area covered by the molecules in the separated condition can only be obtained by the evaluation of the corrections for the area covered and the lateral attractions between molecules, and comparison with the compression curves of a fully expanded film. As the evaluation has not yet been carried out, only the order of magnitude of the area covered can be obtained. Since the curve of the equation $p(A-42) = 7\cdot2$, which is plotted in fig. 1, is so far to the right of the experimental curves, it does not seem probable that the molecules in the expanded film can actually cover an area much greater than $21\cdot0$ Å.U., even when separated from each other; therefore they must probably be vertically arranged.

Other considerations point in the same direction. If the molecules were much inclined to lie flat on the surface, the "b" correction would be much greater for long molecules than for short. This is not the case experimentally, since expanded films of long molecules actually occupy smaller areas than those of short. It is very difficult to account for the approximate equality of the "b" correction when the molecules are of widely differing lengths unless the orientation is substantially vertical.

9. *The Orientation of Unsaturated Acids.*

Langmuir suggested originally, that the tendency of oleic acid to occupy on the surface an area about double that of palmitic was due to the double linkage half-way up the chain being itself attracted to the water, and therefore providing a second point of attachment. The expanded films of oleic and the other unsaturated acids, however, have compression curves very much like those of the saturated acids, such differences as exist being very likely due to the correction for the lateral attraction between molecules being somewhat less for these substances than for the saturated acids. Therefore the "*b*" corrections are of the same order of magnitude, and it follows from the arguments in the preceding paragraph that the orientation of these substances also is practically vertical. The argument, therefore, that the molecules double up, so that the unsaturated linkages in the middle of the chains are in contact with the water, entirely loses its foundation; and the reason why it was at first advanced is seen to be that the distinction between condensed and expanded films was not then clearly recognised.

In a letter to 'Nature' (Part II, Reference 4) I pointed out that on the assumption of the molecules bending so as to bring the double linkage into contact with the water, the greater ease with which oleic rather than elaidic occupied the larger area was evidence in favour of the "cis" configuration for oleic and the "trans" for elaidic acid. Since the assumption is now proved incorrect, the films do not afford independent evidence at present as to the stereochemical configuration of these substances. It can only be said that the lateral attraction of the oleic molecules is less than that of the elaidic, and similarly the attraction of the erucic molecules is less than that of brassidic. This fact, if the considerations in the next paragraph are correct, is connected with the relationships between the melting points of the crystals of the isomers.

10. *Evidence available, from the Study of the Films, and the Melting Points of the Crystals, as to the Crystal Structure of Fatty Acids and their Esters.*

In Table III are given the melting points of the esters of palmitic acid with various alcohols. As the size of the alcoholic group increases, the melting point first diminishes very rapidly from that of the acid; then it is lowered more slowly, and finally begins to rise and continues to do so up to the highest member of which there is a record. The melting points from propyl to octyl palmitates are determined on my preparations, no determinations being apparently recorded previously. These determinations

are accurate enough for the present argument, but should not be taken as standard values, since no analyses have been done of these compounds, and although the alcohols were probably of high purity, in one or two instances they may have been insufficiently dehydrated.

There are two other important relationships; the melting points of the acids and esters rise with increase in the length of the hydrocarbon chains; and the melting points of the acids and esters with an even number of carbon atoms in the molecule lie on one regularly ascending series, the odd members lying on another with melting points about 7° lower.

In the films the explanation of the steady increase in the expansion temperature with length of chain was shown to be due to the chains lying side by side, and attracting one another laterally; it is probable, therefore, that in the crystals also the chains lie alongside, over some considerable part

Table III.—Palmitic Acid and its Esters.

Substance.	Melting point of crystal.	Temperature of half expansion on dilute HCl.
	°	•
Free acid	62·5	28·5
Methyl ester	30	27·5
Ethyl „	25·5	13
n-Propyl „	15–16	below 5
n-Butyl „	13–14	below 5
iso-Butyl „	19–20	Unknown.
iso-Amyl „	11–12	„
n-Octyl „	24–25	below 5
n-Dodecyl ester*	41	Unknown.
n-Tetradecyl ester................................	48	„
Cetyl ester.......................................	53–54	„
n-Octadecyl ester	59	„

* The last four determinations are taken from Krafft, 'Ber. Deutsch. Chem. Ges.,' vol. 16, p. 3017.

of their length. The influence of the size of the alcoholic group on the crystal melting probably indicates that there is a second force of great importance concerned in holding the crystal together, namely the attraction of the polar groups for one another; this is paralleled in the films by the attraction of the polar groups for the water as well as for one another.* This attraction between polar groups appears to be diminished by the introduction of small esterifying groups, such as ethyl or methyl. When the hydrocarbon chain of the alcoholic part of the molecule exceeds about seven carbons in length, probably these long chains supply a second stabilising force.

* The latter part of this section was re-written June 29.

These facts form some guide as to the possible arrangements of the molecules within the crystals; it is assumed that the attractions do not extend to distances much greater than the interval between adjacent atoms, or, at any rate, are much more intense within these distances than beyond. In the acids, and the lower esters, the hydrocarbon chains must lie side by side, and the oxygen-containing groups of several molecules also must lie close together. A possible arrangement would be for the polar groups of a number of molecules to be arranged together in a clump, as a core surrounded by a shell of hydrocarbon chains. A perhaps more probable arrangement has been suggested to me in conversation by Prof. Lowry, F.R.S., that the molecules are in parallel layers with the hydrocarbon chains alongside and polar groups in each layer all in the same direction; the polar groups of one layer in contact with those of the next, and the hydrocarbon ends touching the corresponding ends of the molecules in the next layer on the other side. The latter arrangement admits of the insertion of alcoholic hydrocarbon chains of any length in the esters, without radically altering the arrangement, in the same line as the chains of the acidic part of the molecules; the former would require a fundamental re-arrangement at about the octyl ester.

11. *The Independence of the Properties of Solubility in the Underlying Solution and Expansion along the Surface.*

In his original paper (Part II, reference 5, p. 1889) Langmuir compared the layer of concentrated solute or adsorbed film in the surface of solutions with a gas, showing that the adsorbed molecules may obey approximately a law $pA = KT$ in the surface. He also showed that the surface monomolecular films of palmitic acid, or condensed films, possess an immeasurably small " vapour pressure" in the surface. In contrasting the two kinds of film, the insoluble acid films which are also condensed, and the "gaseous" films of adsorbed substances, he said: " The smallness of this (vapour) pressure for the higher fatty acids must be due to attractive forces between the molecules powerful enough to prevent their separation. These same forces tend to prevent the film from evaporating from the surface into the vapour phase, and from going into solution in the water. There are thus intimate relationships between the lowering of surface tension produced by fatty acids and the vapour pressures and solubilities of these substances."

This way of stating the relationships gives the impression that it is the lateral adhesion between the molecules which prevents the films dissolving, and that an isolated molecule on the surface would dissolve very rapidly. I do not think there is any *a priori* reason for taking this view, although, no

doubt, a long hydrocarbon chain tends both to diminish solubility and to cause the molecules to adhere together on the surface. My experiments have shown a certain amount of independence between the tendency to dissolve and to separate laterally on the surface. Thus films of palmitic acid remain practically insoluble for some 20° above the temperature of expansion, but with cetyl alcohol, the solubility is marked some distance below the temperature of expansion.

It does not seem legitimate to state, *a priori*, what will be the relation between the tendency to dissolve and the tendency to expand; but as both these quantities are now capable of independent measurement, I hope to obtain some results on this problem in the near future.

Diffusion and Intertraction.

By C. G. SCHONEBOOM.

The starting-point of this investigation was the phenomenon which Sir Almroth Wright described in the 'Proceedings of the Royal Society,' Series B, vol. 92. The original experiment is conducted by putting 5 or 8 per cent. NaCl in a test-tube or flat glass cell and allowing some blood serum to run slowly on the top of the NaCl. As soon as the fluids are brought into contact, a mass movement is started, the upper fluid being carried down into the lower and the lower into the upper. The characteristic appearances so produced are well described by the terms intertraction or pseudopodial interpenetration. By colouring the serum with a trace of some dyestuff (*e.g.*, eosin) the intertraction phenomenon is easier to follow; or by having a layer of tannic acid or sulpho-salicylic acid in NaCl solution on the bottom, one sees after a short time (some minutes) a heavy precipitate in the lower interface.

This system, serum on NaCl solution, presents a typical example of the intertraction phenomenon, as will be described in the following experiments, in so far that in the case of serum and NaCl solution both fluids are, so to speak, active and penetrate each other quickly, so that after some time (10 to 30 minutes) the contents of the vessel are a homogeneous mixture, as can readily be seen if eosin be used in the serum. This result, the homogeneous

mixing, is completed by ordinary diffusion, which very soon sets in after the intertraction has begun, from the numerous streams and droplets of the serum which come down in the NaCl solution.

One suggestion put forward was that the cause was a water-drawing action by the salt. This view might appear to be supported by Nägeli's suggestion that the colloid particles possess a watery envelope (partly bound chemically as hydrate water and partly as adsorption water).

In view of the above, I started the investigation of various colloids: egg albumen, blood serum, gelatin, gum arabic, tannic acid, and starch. All these give a typical intertraction phenomenon and seem to give support to the suggestion that the salt would abstract water from the colloid, and thus increasing the weight, induce the intertraction.

At the outset I found that for producing intertraction it was not necessary to use salt (NaCl) or other electrolyte. Organic compounds such as urea, chloral hydrate, thiosiamin, phenozason, and acids such as oxalic, citric, tartaric, etc., also produced intertraction with colloids.

An experiment showing this is set forth in Table (Diagram) I below. The fact that electrolytes were not essential to the production of intertraction makes it possible to produce this phenomenon with inorganic colloids also, such as Prussian blue, and with aniline dyes, which are precipitated by concentrated solutions of electrolytes.

Table (Diagram) I.—Gum Arabic Solutions superposed on Quinine Hydrochlorate (Acid Salt) solutions.

Gum arabic percentages	0	3	6·25	12·5	25	37·5	50
25					↓	30	60
18·75					30	60	120
12·5				↓	30	60	
6·25			↓	30	60		
3		↓	45		500		
1·5		45	60	180			

Quinine percentages.

↓ indicates that the upper solution is heavier and comes down directly by gravity. The figures 30, 60, etc., represent the number of seconds which elapse between the superposition of the gum arabic solution and the starting of pseudopodial intertraction.

The further point then emerged that intertraction phenomena are obtained not only with colloidal solutions, but also with *all* inorganic and organic

compounds without any exception, provided always that the substances in question are sufficiently soluble in water and that there is not too great a difference in specific gravity between the upper and lower solutions.

Table (Diagram) II gives an example, taken at random, of the wide range in concentration with which the intertraction phenomenon occurs. In point of fact, solutions of all chemicals (provided they do not react chemically) are found to give approximately the same picture when set out graphically, differing only in the range of concentrations in which the intertraction occurs.

Table (Diagram) II.—HCl 0·1 mol.–2 mols. on KNO_3 0·1 mol.–1 mol.

HCl (mol.)	0·1	0·2	0·3	0·4	0·5	0·6	0·7	0·8	0·9	1 m.
2					↓	+	+	+	+	+
1·9					+	+	+	+	+	+
1·8					+	+	+	+	+	+
1·7					+	+	+	+	+	+
1·6				↓	+	+	+	+	+	+
1·5				+	+	+	+	+	+	+
1·4				+	+	+	+	+	+	+
1·3				+	+	+	+	+	+	+
1·2			↓	+	+	+	+	+	+	+
1·1			+	+	+	+	+	+	+	+
1			+	+	+	+	+	+	+	+
0·9			+	+	+	+	+	+	+	+
0·8		↓	+	+	+	+	+	+	+	+
0·7		+	+	+	+	+	+	+	+	+
0·6		+	+	+	+	+	+	+	+	+
0·5		+	+	+	+	+	+	+	+	+
0·4	↓	+	+	+	+	+	+	+	+	+
0·3	+	+	+	+	+	+	+	+	+	+
0·2	+	+	+	+	+	+	+	+	+	+
0·1	+	+	+	+	+	+	+			
0										

(vertical label "strong position" appears at the KNO₃ 0·5 and 1 m. columns)

KNO_3.

↓ indicates that the upper fluid is heavier and comes down direct by gravity.
+ indicates intertraction.

The next question which presented itself was whether the size of the molecule exerts any effect on the phenomenon. Here I employed both aniline dyes and alkaloids and simple inorganic and organic substances. Experiments showed that the size of the molecules has no influence.

In connection with the suggestion that the intertraction phenomenon might depend on the withdrawing of water, I paid special attention to the varying amount of hydrate water, which is supposed to be weakly held by most salts, bases, and acids, specially in dilute solutions (hydrate theory of Harry Jones and others). For example, salts like disodium phosphate, with a maximum of about 325 hydrate water molecules round them, gave the intertraction phenomenon as well as those which, like the simple potassium salts, are supposed to collect no, or very little, hydrate water round their molecules or ions.

The presence, or absence, of hydrate water, was found to be without any influence on the intertraction phenomenon. The same thing was found to hold true with organic compounds investigated from this point of view. Intertraction is obtained both with glucose, lactose, tartaric acid, citric acid (substances which have little or no hydrate water), and with fructose and cane sugar (substances which have much hydrate water). But in one of the earlier experiments the dehydration was very conspicuous in connection with intertraction. In the experiment in question, cobalt chloride solution (2-2·5 molar) was superposed upon a saturated calcium chloride solution. Here after a short interval (from a few seconds to 1 or 2 minutes), *blue* streams and droplets come down from the *red* cobalt solution into the calcium chloride solution, the change of colour being due to a conversion of the cobalt chloride + $6H_2O$ into the cobalt chloride + $1H_2O$. It was, however, established by taking weaker solutions of the calcium chloride and the cobalt chloride that the intertraction phenomenon occurred also, and to an equal extent, without any colour change, so that the dehydration obtained in strong solutions stands in no causal connection with the intertraction phenomenon.

Final and conclusive evidence that intertraction has nothing to do with dehydration, and occurs quite independently of it, was furnished by the fact that intertraction is also obtained when, instead of water, organic solvents (such as glacial acetic acid, ethyl acetate, amyl acetate, glycerol, amyl alcohol, aniline, pyridine) are employed. Reflection will show that the only forces which can come into operation are forces of surface tension.

Two observations, in particular, seemed to point clearly in that direction. The first was made in the course of an experiment which must here be described in detail. It consists in taking a double series (A and B) of ten

test-tubes with graduated sodium chloride solutions, ranging from 0·90 molar, 0·91, 0·92, etc., to 1 molar sodium chloride, and adding to the tubes of series B some drops of a solution of eosin in water, having the same specific weight as the sodium chloride solutions. Then the *coloured* sodium chloride solutions are superposed on the uncoloured solutions, in such a way that the 0·9 coloured solution is put on the 0·91, or 0·92, uncoloured solution, and so on in series; the coloured solutions will then be seen to go down almost immediately after the fashion which I have called pseudopodial intertraction.

When the conditions are varied and the coloured 0·9 solution is placed on the 0·95, or any denser uncoloured solution, intertraction is suppressed, because the forces engaged in intertraction are, in this case, unable to overcome the effect of the larger difference in specific gravity.

The second observation relates to colloidal gold and silver solutions superposed on solutions of urea (varying from 0·5–5 per cent.). When such experiments are carried out, it is found that intertraction is obtained with colloidal solutions which are prepared by chemical means, but the phenomenon fails to occur with solutions prepared by the electric method (direct current arc).

The point of these two experiments is, that the eosin employed in the first experiment is a powerful depressor of surface tension, and in the second experiment, where we are dealing with chemically prepared colloidal gold and silver solutions, we have traces of salts (gold chloride, potassium carbonate, etc.), and organic substances (tannic acid, alcohol, formaldehyde), which alter the surface tension, while in the case of the electrically prepared solutions we have the colloidal particles suspended in pure water (possible traces of oxides can be left out of consideration).

The view that intertraction is dependent on certain relations of surface tension is strongly supported by a passage in an article by Clerk Maxwell on "Capillarity," in the 'Encyclopædia Britannica,' 11th edition, p. 259. This passage, here cited in the form in which it appears in his collected papers, runs as follows:—

"If this quantity (the interfacial tension) is positive, the surface of contact will tend to contract, and the liquids will remain distinct. If, however, it (the interfacial tension) were negative, the displacement of the liquids, which tends to enlarge the surface of contact, would be aided by the molecular forces, so that the liquids, if not kept separate by gravity, would at length become thoroughly mixed.

"No instance, however, of a phenomenon of this kind has been discovered, for those liquids, which mix of themselves, do so by the process of diffusion, which is a molecular motion, and not by the spontaneous puckering and

replication of the bounding surface as would be the case if T [the interfacial tension] were negative."

It is of singular interest to find the phenomenon of intertraction here predicted and quite accurately described in advance. Anyone who has observed intertraction will acknowledge that we have, in the above description, an accurate word picture of this phenomenon. After a few seconds one sees the puckering beginning, and in many cases the surface layer of the active fluid is replicated. This is the phenomenon which Sir Almroth Wright called "pseudopodial intertraction."

In addition to this typical intertraction there is another form of mixing—"simple intertraction," which is intermediate between pseudopodial intertraction and the well-known slow processes of diffusion.

Simple intertraction occurs when the difference of the specific gravity of the two superposed fluid layers is greater, and also when the relations of the surface tensions are different from those under which the pseudopodial intertraction happens. There is a gradual transition between pseudopodial intertraction, simple intertraction, and diffusion, as is illustrated in the following experiments:—

A series of long test-tubes (surrounded by a water mantle to eliminate convection movements, caused by temperature differences) are filled to the same height with hydrochloric acid (1 molar). On the hydrochloric acid we superpose in the first tube water, and then, in their order, sodium chloride solutions of the following strengths: 0·001, 0·01, 0·02, 0·04, 0·06, 0·08, 0·1, 0·2, 0·3, and 0·4 molar. To these solutions is added a trace of methyl orange, to act as an indicator of the progress of the acid.

It is now found that in the—

0·4 mol. NaCl, the HCl rises	60 mm. in 1 minute	} Advancing in the form of
0·3 " "	60 mm. in 12 minutes	pseudopodial intertraction.
0·2 " "	progressively slower	
0·1 " "	" "	Advancing on a level front
0·08 " "	" "	by what has been called
0·06 " "	" "	above interpenetration by
0·04 " "	" "	simple intertraction.
0·02 " "	" "	
0·01 " "	40 mm. in 12 hours.	
0·001 " "	39 " "	
Water, the HCl rises 36 mm. in 12 hours.		

We see from the above Table that hydrochloric acid rises in the tubes which contain the weakest salt solutions practically at the same rate as in pure water. Here the dividing line between the red and yellow colour stands after 12 hours about 40 mm. above the base line. In the stronger solutions

(*e.g.*, in the 0·1 molar sodium chloride) the hydrochloric acid has risen to the top—in 12 hours more than 200 mm.*

The general results such as those in the experiments above are obtained also with the various acids and bases and with the numerous salts which were investigated. While it holds true that these three forms of mixing (that is diffusion, simple intertraction, and pseudopodial intertraction) are obtained with all substances, it is to be noted that the range of concentrations which give the simple and pseudopodial intertraction is very narrow in some combinations, in others it is extremely wide.

For example, we take a series of sixteen test-tubes and fill them with sodium chloride solutions in progressive concentrations, ranging from 0·01 to 4 molar. Into each test-tube is put a filtered saturated solution of eosin (specific gravity of 1050), in the first eight tubes under the salt solution, and in the last eight tubes on the top of the salt solutions.

Except in the tubes of the very lowest concentrations, penetration by intertraction takes place, and what is specially striking in the experiments is that intertraction occurs with great rapidity—the eosin solution being carried up or down despite the very great differences in specific gravity.

Table III.

Layers.	Diffusion (H_2O superposed on HCl).	Intertraction (2 mol. HCl superposed on 1 mol. NaCl).					Intertraction (1 mol. KNO_3 on 1·4 mol. KCl).
	After 24 hours.	After 3 mins.	After 6 mins.	After 1 hour.	After 14 hours.	After 24 hours.	After 6 mins.
1	0	—	—	47·0	22·5	21·5	0·2
2	0	4·4	3·5	4·1	8·25	9·5	0·25
3	0	0·9	1·3	4·05	5·8	7·0	0·3
4	0	0·45	0·75	3·95	7·65	6·6	0·4
5	0	0·45	0·7	3·9	6·8	6·7	0·5
6	1·3	0·3	0·8	4·25	7·4	7·2	0·8
7	18·3	0·35	0·65	3·9	6·8	6·3	3·5
8	2 mol. HCl	0·4	0·9	4·0	6·8	6·4	1·4 mol. KCl
				75·15	71·1	71·9	

The figures indicate the number of cubic centimetres of 1/10 molar sodium hydroxyde necessary to neutralise the hydrochloric acid, and in the case of the KCl-KNO_3 combination 1/10 molar silver nitrate.

* In this connection I may point out, that the quickened diffusion of hydrochloric acid (in sodium chloride solution) diffusing into sodium chloride solution of the same concentration (as observed first by Arrhenius and studied by Abegg and Rose) and satisfactorily explained by the ionic theory, is *not* the cause in the experiments described above, as the movement of the hydrogen ion in Arrhenius's experiments is only accelerated three and a half times, while the progress of the hydrochloric acid is here ± 2,000 times more rapid than in the ordinary diffusion.

Thus far we have investigated only the rate at which mixing by inter-traction occurs. It seemed desirable to get some idea of the amount of the chemical substances transferred from the one intertracting fluid into the other. A few illustrative experiments are given in Table III.

Concentration :—MgSO₄ (1 molar) upon CoCl₂ (1 mol.).
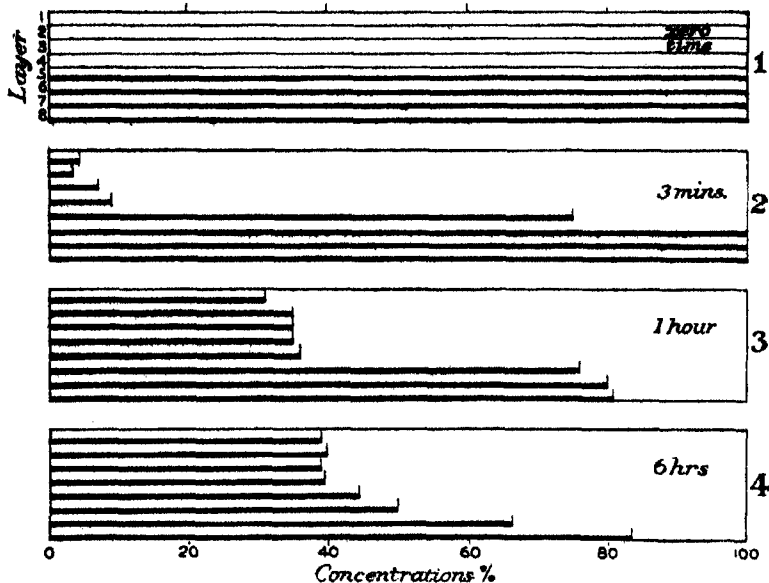
Concentration :— MgSO₄ 0·9 mol. upon Co Cl₂ 1 mol
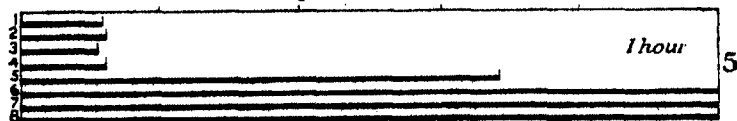
Concentration :— MgSO₄ 0·6 mol. upon Co Cl₂ 1 mol.
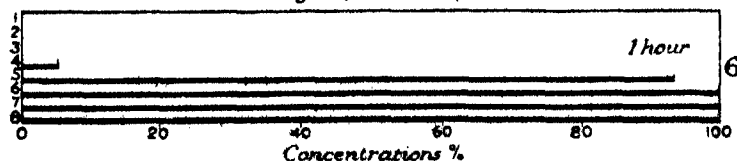
Length of black lines shows degree of concentration of CoCl₂.

For the purposes of the analysis the column of fluid, which was 20 cm. high, was divided into eight sections, about 4 c.c. of fluid being contained in each. In Table III are set forth a series of results which apply to hydro-chloric acid diffusing upwards into water (section 1). In the second section we have the results obtained by hydrochloric acid penetrating by inter-

traction into sodium chloride solution, and in the third potassium chloride penetrating by intertraction into potassium nitrate.

In the diagram are set out a series of results applying to magnesium sulphate superposed on cobalt chloride. It is divided into sections; in the first section (1–4) is depicted the progress of the intertraction, the analysis having been made after three different time-intervals. The lower sections (5 and 6) of the diagram are to be read in relation to No. 3.

In conclusion, I have much pleasure in expressing my thanks to the Committee of the Inoculation Department for the facilities afforded to me for the carrying out of this research, and to Sir Almroth Wright for the interest he has taken in this research and his kind assistance in framing this paper.

The Absorption Spectrum of Potassium Vapour.

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(Communicated by Prof. A. Fowler, F.R.S. Received June 29, 1922.)

[Plate 5.]

1. *Introductory.*

In connection with the investigation of the vacuum arc spectrum of potassium,[*] which was undertaken mainly to improve the existing measures, it was found that the type of lamp used in that experiment was unsuitable for the production of the higher members of the series. Already Wood[†] has shown that the principal series of sodium is much more complete in the absorption than in the emission spectrum, and has extended the series up to $m = 57$. Bevan[‡] repeated the experiments with the other alkali elements and was able to extend the principal series in each case very considerably. In view of the importance of obtaining accurate measures of these lines and a possible extension of the series, so that they may afford data which will help to throw some light on the question as to the nature of the formula giving series lines, it was thought desirable to repeat the experiment of Bevan with instruments of greater dispersion. The results which have been accomplished in the repetition of the work may be briefly summarised as follows :—

(1) The number of members of the series has been raised from twenty-four

[*] 'Roy. Soc. Proc.,' A, vol. 99, p. 69 (1921).

[†] R. W. Wood, 'Astrophys. Journ.,' vol. 29, p. 97 (1909); R. W. Wood and R. Fortrat, 'Astrophys. Journ.,' vol. 43, p. 73 (1916).

[‡] 'Phil. Mag.,' vol. 19, p. 195 (1910).

to forty-two. (2) The first seven members of the series have now been resolved into their components as compared with five in previous investigations. (3) Besides the absorption of the lines of the principal series, new lines have been found to be absorbed at somewhat higher pressure which seem to have no correspondence with the known lines in the emission spectrum. (4) An important result of the experiments is the observation of the absorption of the two combination lines $1s$—$2d$ and $1s$—$3d$, the first as a pair confirming the presence of a satellite to the lines of the diffuse series, and the second as an unresolved line.

2. *Experiments.*

The metallic potassium was vapourised in a tube of steel, about 20 inches in length and 1 inch in diameter, heated electrically, so as to obtain proper control over temperature. The ends of the tube were closed with thin quartz lenses, attached with sealing-wax and kept cool by circulation of cold water through two jackets fitted on the ends of the tube. Previous to heating, the tube was exhausted by a Gaede pump, and during the experiment the vapour pressure of potassium was maintained nearly constant by a make-and-break arrangement in the heating circuit, which secured the necessary control. As the source of light, the white-hot crater of an ordinary carbon arc, maintained at 110 volts and about 12 ampères, was used. Besides giving out a strong continuous spectrum it emitted a few iron and other lines, which were used as comparison lines with advantage and provided the surest check against any mechanical shift. The temperature of the tube and the resulting vapour density of potassium were regulated according to the portion of the series under investigation. Preliminary experiments with a small quartz instrument revealed the fact that for the first few members the pressure should not exceed 8 mm. in order to obtain lines sharp enough for good measures. At this low density, however, members higher than 15 were not absorbed. Keeping the temperature low by intermittent exhaustion and raising the temperature of the tube by continuous heating, it was possible to extend the series up to $m = 26$, while maintaining the lines sharp. Absorptions of still higher members as fine lines were secured at a pressure of about 37 mm. at the sacrifice of the sharpness of the lines constituting the earlier members. At this stage the new lines also appeared.

Measurements were made on photographs taken in the second order spectrum of the 10-foot concave grating, giving a dispersion of about 2·8 Å.U. per millimetre. The wave-lengths of the reference iron lines were taken from the table given by Burns.

The new measures are collected in Table I :—

Table I.—Principal Series of Potassium. 1s—mp, 1s=35008·48.

λ I.A.	ν (vac.).	Δν.	mp₁,₂.	m.	νobs. − νcal.
*7664·94	13042·82	57·71	21965·66	(1)	0·00
99·01	12985·11		22023·37		
†4044·140	24720·18	18·69	10288·30	(2)	0·00
47·201	701·49		306·99		
†3446·722	29004·70	8·15	6003·78	(3)	−2·53
47·701	8996·55		11·93		
3217·176	31074·22	4·43	3934·26	(4)	0·07
16·633	060·79		38·69		
3101·806	32221·96	2·25	2778·52	(5)	0·09
02·023	227·71		80·77		
3034·780	32941·76	1·65	2066·72	(6)	0·19
34·932	40·11		68·37		
2992·140	33411·18	1·11	1597·30	(7)	0·28
92·240	10·07		98·41		
2963·260	33736·78		1271·70	(8)	0·08
43·718	33972·28		1086·20	(9)	0·17
2927·602	34147·68		860·60	(10)	0·04
2916·114	34282·20		726·28	(11)	0·11
2907·208	34387·28		621·20	(12)	−0·05
2900·126	34471·18		587·30	(13)	−0·06
2894·407	34539·29		469·19	(14)	
2889·788	34595·09		413·39	(15)	0·01
2885·857	34641·62		366·86	(16)	0·10
2882·814	34680·60		327·88	(17)	0·06
2879·864	34713·70		294·78	(18)	0·04

λ I.A.	ν (vac.).	mp.	m.	νobs. − νcal.
2877·509	34742·11	266·87	(19)	0·08
2875·494	34766·46	242·02	(20)	−0·01
2873·743	34787·64	220·84	(21)	−0·04
2872·214	34806·15	202·33	(22)	−0·06
2870·865	34822·51	185·97	(23)	−0·03
2869·608	34837·05	171·43	(24)	0·09
2868·627	34849·80	158·68	(25)	0·03
2867·676	34861·24	147·24	(26)	0·06
2866·832	34871·50	136·98	(27)	0·10
2866·075	34880·72	127·76	(28)	0·11
2865·407	34888·84	119·64	(29)	−0·06
2864·778	34896·52	111·96	(30)	0·09
2864·213	34903·38	105·10	(31)	0·11
2863·703	34909·60	98·88	(32)	0·10
2863·244	34915·18	93·30	(33)	0·00
2862·823	34920·33	88·15	(34)	−0·06
2862·421	34925·23	83·25	(35)	0·04
2862·069	34929·54	78·94	(36)	−0·05
2861·71	34933·89	74·59	(37)	0·05
2861·38	34937·92	70·56	(38)	0·50
2861·07	34941·73	66·75	(39)	0·53
2860·83	34944·64	63·84	(40)	0·51
2860·51	34968·66	59·82	(41)	1·48
2860·32	34951·10	57·38	(42)	1·15

* Measures taken from Meggers.
† Vacuum arc measurements.

3. *Regularity of the Series.*

It is well known that the frequencies of any of the recognised series can be approximately given by a formula of the type $\nu = A - N/[f(m)]^2$. A convenient form of $f(m)$ is that suggested by Hicks, viz., $f(m) = m + \alpha + \beta/m$. Assuming N to be known, the limit A of the series, as well as its other constants, are usually calculated from the lines giving the earlier members of the series. The actual calculated value of A then not only suffers from the errors of observation of the three lines, but also depends to a considerable extent on the form of $f(m)$ employed and the value of the constants α, β. It is evident that in the case where many members of a series are known, the limit might be best obtained from the higher members. And although it may be objected that these higher members, being in the ultra-violet small observational errors in wave-lengths, are multiplied by large factors in the wave numbers, by taking a sufficient number of them into account the mean will give a more trustworthy result than is obtainable by any other means. Prof. Nicholson[*] has suggested a method for the accurate determination of the limit of the series which involves the above mode of treatment. The method requires for its application a preliminary formula, for example, of the Hicks type, for the expression of the series. If the series is represented by

$$\nu_m = A - N/(m + \alpha + \delta)^2,$$

then

$$\nu_m = A - \frac{N}{(m+\alpha)^2}\left[1 - \frac{2\delta}{m+\alpha} + \frac{3\delta^2}{(m+\alpha)^2} - \ldots\right].$$

The fourth term of the convergent series is $3N\delta^2/(m+\alpha)^4$, and since N is about 10^5, this cannot exceed a certain value which will affect the significant figure in A beyond a certain value of m depending on the value of δ used. For all the lines beyond that value of m,

$$\nu_m = A - \frac{N}{(m+\alpha)^2} + \frac{2N\delta}{(m+\alpha)^3},$$

whence,

$$A = \frac{(m+1+\alpha)^3\,\nu_{m+1} - (m+\alpha)^3\,\nu_m + N}{(m+1+\alpha)^3 - (m+\alpha)^3}.$$

If N is known, this formula would permit a determination of the limit of the series from any pair of consecutive lines. Taking $N = 109678\cdot31 + \Delta N$, where ΔN represents the difference of N for potassium from that for hydrogen determined accurately by W. E. Curtis,[†] A can be calculated and will include a known and an unknown part involving ΔN. The formula adopted by Prof. Fowler[‡] for the principal series of potassium is

$$\nu(m) = 35005\cdot88 - N/(m + 1\cdot296281 - 0\cdot061661/m)^2.$$

[*] J. W. Nicholson, 'Roy. Soc. Proc.,' A, vol. 91, p. 255 (1915).

[†] W. E. Curtis, 'Roy. Soc. Proc.,' A, vol. 90, p. 605 (1914).

[‡] A. Fowler, 'Report on Series in Line Spectra,' p. 101.

Taking these values of the constants, it can be shown that for lines beyond $m = 9$, the fourth term mentioned above is negligible.

Considering some of the lines beyond $m = 9$, the values of A have been calculated by Nicholson's method, giving the results shown in Table II.

Table II.

Calculated from lines $m =$	A.	
10, 11	35008·38	$+ \Delta N/418$
13, 14	35008·48	$+ \Delta N/657$
14, 15	35008·08	$+ \Delta N/749$
19, 20	35008·15	$+ \Delta N/1297$
24, 25	35009·27	$+ \Delta N/1996$
25, 26	35008·89	$+ \Delta N/2154$
26, 27	35009·99	$+ \Delta N/2318$
28, 29	35006·79	$+ \Delta N/2663$
31, 32	35007·88	$+ \Delta N/3226$
33, 34	35007·78	$+ \Delta N/3632$

No value of ΔN can be found which makes the general deviations from equality any smaller than they are for the calculated parts at present. This does not necessarily mean that $\Delta N = 0$, but that the method is not suitable for the calculation of ΔN with the available observations. But as any reasonable value of ΔN will only affect the second decimal figure in the value of A, ΔN may be assumed to be zero. The mean value of A thus obtained is $A = 35008·48$.

With this limit and any two other lines it is possible to calculate the series, but it is found that unless the earlier members are used for the calculation of constants, the difference in the observed and the calculated wave numbers far exceeds the limits of observational error, perhaps due to the important part which ΔN plays for these earlier members. A formula which represents the whole series very closely has been obtained with the above limit and the stronger components of the first and second lines, namely,

$$p_1(m) = 35008·480 - 109736·1 \Big/ \Big(m + 1·29667 - \frac{0·06154}{m}\Big)^2.$$

With the value of $N (= 109736·1)$ obtained by taking the mass correction of the nucleus of potassium into account, the agreement between the observed and the calculated values (shown in Table I) is somewhat better than when the value of N for hydrogen (109678·3) is used. Except for the deviation shown at $m = 3$, which is rather abnormal, and the last four members ($m = 39$ to 42), the agreement is within the errors of observation, which are believed to be not greater than 0·01 A. The deviations of the higher members ($m = 39$ to 42) are supposed to be real, as the change in the value of N due to any perturbation, or those of the constants α and β, have very little effect for higher values of m. It may be mentioned here that the

principal series of sodium also shows similar deviations for the last few lines, and Prof. Hicks* has expressed his doubts whether they actually belong to the typical p series. It is, however, possible to extend an idea of Prof. Sommerfeld to these higher members which may explain the observed deviation. Prof. Sommerfeld, with a view to explaining the continuous spectrum which usually appears† at the end of the series, has put forward the theory that, when the radiating electron is knocked out of the atom, it comes into collision with other free electrons or atoms, and consequently, when it falls back to the limiting orbit and forms part of the atom, the extra energy received during the collision has also to be taken into account.

As the electron can acquire any velocity during such collision, the extra energy ($\frac{1}{2}\mu v^2$), where μ is the mass of the electron and v the velocity acquired, may have any value from zero upward. Consequently the electron, in falling to the limiting orbit, would not give rise to a line (the limit of the principal series), as is to be expected from Bohr's theory, but a continuous spectrum stretching on the more refrangible side of the limiting line. Now the condition of the electron, owing to the very weak influence of the nucleus in any of the very high orbits (almost approaching the limit), is not very different from one entirely removed from the atom. So that it possibly acquires extra energy in a similar way. And if the energy received be not sufficient to ionise the atom or to raise the electron to higher orbits, then there will be an increase in the amount of energy radiated. The total effect of this would be to broaden the lines (as they are known to be), with the consequent displacement of the line on the more refrangible side. In both sodium and potassium, the observed frequency is higher than the calculated one for the last few lines.

4. *Absorption of Lines other than the Principal Series.*

Besides the absorption lines of the p series, several new lines were absorbed at higher pressure, of which no traces could be found at low pressure. The experiments on absorption were carried on at five different pressures: 2·5 mm., 5 mm., 20 mm., 37 mm., and 46 mm. These new lines made their first appearance at 20 mm. pressure, strengthening in intensity, and becoming diffuse as higher pressures were reached. Up to $m = 6$, lines were observed on both sides of the p series lines. At $m = 2$, the lines are far removed from the p series line, but they gradually approach and finally coalesce with the p series lines with decreasing intensity as $m = 7$

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* W. M. Hicks, 'Astrophys. Journ.,' vol. 44, p. 239 (1916).

† It is most striking in the case of the Balmer series of hydrogen, especially as it appears in some of the stars.

is reached. At $m = 6$ another set of lines appear, which run parallel with the p series lines in the scale of oscillation frequency and on their more refrangible side.

These lines seem to have no correspondence with the emission lines of potassium, and attempts to correlate them have not been successful. Their wave-lengths and wave numbers corrected to *vacuo* are collected in Table II. The wave-lengths of the nearest p series lines are also given, in order to show their divergences from them.

Table III.

Converging Set.				Parallel Set.			
Designation.	λ I.A.	ν (vac.).	Δν.	Designation.	λ I.A.	ν (vac.).	Δν.
New	Merged into the broad violet band.			p_1 (6)	3034·780	32941·76	19·33
p_2 (2)	4047·201			,New	3033·0	961·09	
p_1 (2)	4044·140	24720·18	113·86	p_1 (7)	2992·140	33411·18	18·88
New	4025·6	24634·04		New	2990·45	480·06	
New	3461·7	28879·2	117·4	p_1 (8)	2963·260	33736·78	17·69
p_2 (3)	3447·701	28996·55		,New	2961·71	745·47	
p_1 (3)	3446·722	29004·70	101·6	p (9)	2942·718	33972·28	17·62
New	3434·7	29106·3		New	2941·19	989·90	
New	3221·8	31029·9	46·9	p (10)	2927·602	34147·68	17·57
p_2 (4)	3217·663	31069·79		New	2926·10	165·25	
p_1 (4)	3217·176	31074·22	32·9	p (11)	2916·114	34280·20	18·88
New	3213·8	31107·1		New	2914·51	01·08	
New	3103·4	32213·4	14·3				
p_2 (5)	3102·023	32227·71					
p_1 (5)	3101·806	32229·96	13·5				
New	3100·5	32243·5					
$p_{2,1}$ (6)	New lines are too feeble to measure.						

5. *Absorption of the Combination Lines* 1s—2d, 2d' *and* 1s—3d.

One of the most interesting results achieved in the repetition of the experiment is the absorption of the two combination lines $1s-2d$ and $1s-3d$. Previous to this only the lines of the principal series have been observed in absorption. According to Bohr's theory the radiating electron is in the $1s$ orbit in the quiescent state of the atom, and the absorption of energy causes its transfer from the $1s$ orbit to the successive orbits. The absorption of practically all the members of the principal series clearly suggests that the energy absorbed in the process is very nearly that required to ionise the atom if not actually ionising it. In the scale of energy, the positions of the d orbits are much nearer to the $1s$ orbit than even the $2p$ orbit. Consequently it was considered very remarkable that the energy sufficient to knock out the electron from the atoms was not sufficient to transfer it to the d orbits.

According to Sommerfeld these lines represent an interorbital transition requiring a change of two units in azimuthal quantum, which is forbidden according to the selection principle of Bohr or Rubinowicz. While the line is well known, its excitation has been thought to be occasioned by the presence of the electrostatic field. In the present case, however, it is difficult to conceive of any external electrostatic field. The possibility of the influence of the electric field due to the neighbouring atoms is also precluded from the fact that these lines were observed at even the lowest pressure (2·5 mm.). Had there been any such field of atomic origin their effect on the bands of potassium, which were simultaneously absorbed, would have been too great to escape notice. Absorption bands of potassium, though faint, were beautifully sharp at 2·5 mm. pressure, and no blurring was noticed till the pressure reached as high as 30 mm., when the flutings merged into a continuous mass owing to the acknowledged Stark effect. The intensity of the combination lines, however, increased with an increase in pressure; but this may mean more than anything else that, at low pressure, owing to the smallness of the number of absorbing atoms, the chances of such extraordinary transfers are very rare. The effect of increase of pressure is to increase the chances by increasing the number of atoms. The possibility of bringing out these transfers, without an external field is proved beyond doubt by the beautiful experiments of Foote and others,[*] who observed the radiation of the combination lines $1s$—$2d$, $2d'$ in the space shielded from the applied electrostatic field—itself very low.

This result and that of Foote and others may, therefore, be pointed to as distinct evidence of contradiction of the selection principle as at present enunciated.

The combination lines $1s$—$2d$ were observed as a pair, as previously recorded,[†] and may be put forward as an indication of regarding the diffuse lines as having a satellite.

The line at about $\lambda 3650$ was photographed with a small quartz spectrograph in the vacuum arc experiment and was recognised as the combination $1s$—$3d$.[‡] This was, however, not included in the previous paper owing to the rough nature of its measure. This was observed as an absorption line in the present experiment, its wave-length having the value—

$$\lambda\ 3648\cdot971, \qquad \nu\,(\text{vac.})\ 27397\cdot19, \qquad \nu_{\text{cal.}}\ 27397\cdot6.$$

The absorption of all the lines, one of whose terms is $1s$, gives an additional

* P. D. Foote, W. F. Meggers, and F. L. Mohler, 'Astrophys. Journ.,' vol. 55, p. 145 (1922).

† 'Roy. Soc. Proc.,' A, vol. 99, p. 69 (1921).

‡ See A. Fowler, 'Reports on Series in Line Spectra,' p. 103.

The Absorption Spectrum of Potassium.
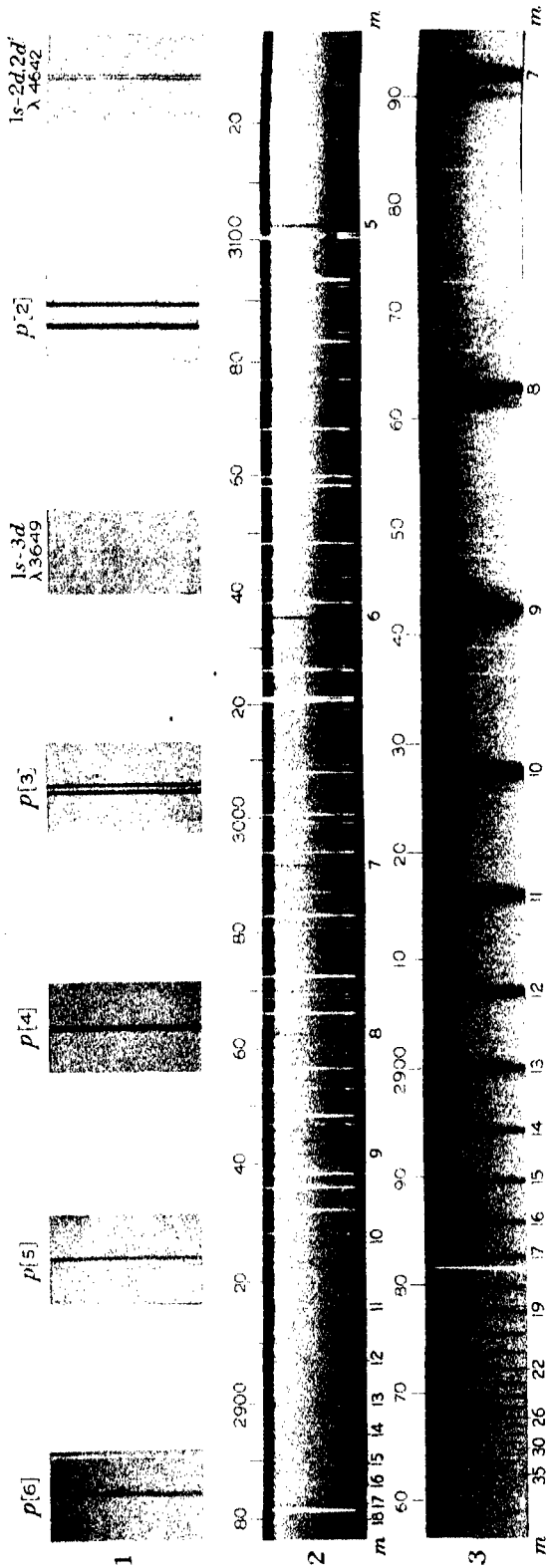
stress to the 1s orbit as being the significant one. The significance of 1s orbit according to Bohr's theory is that it represents the orbit of the electron in the normal state of the atom. Consequently the chances for all radiations one of whose terms is 1s are very great. Increasing, therefore, the chances alone by appropriate experiments, the absorption of lines corresponding to other interorbital transfers may possibly be obtained.

The absorption *bands* of potassium have also been photographed and will form the subject of a separate communication.

Summary.

1. The principal series lines up to $m = 42$ have been observed as absorption lines and their wave-lengths accurately measured. The series equation shows satisfactory agreement between the observed and the calculated values with the exception of deviations for the last few lines for which a possible explanation has been given.

2. The first seven members of the series have been resolved into their components as compared with five in previous investigations.

3. Besides the absorption of the lines of the principal series, new lines have been found to be absorbed at higher pressures, which seem to have no correspondence with the known lines in the emission spectrum.

4. The combination lines $1s$—$2d$ and $1s$—$3d$ have been found to be absorbed, the first as a pair, confirming the presence of a satellite to the lines of the diffuse series. Their appearance in the absorption spectrum gives distinct evidence of contradiction of the selection principle.

In closing, my best thanks are recorded to Prof. A. Fowler, F.R.S., for his helpful interest in the work.

DESCRIPTION OF THE PLATE.

Fig. 1.—Showing the combination lines $1s$—$1d$, $2d'$; $1s$—$3d$, and the earlier members of the principal series in order of decreasing wave-length. p [6] is from an enlargement of a second order negative, all others are from that of a first order.

Fig. 2.—Showing the absorption of the principal series lines from $m = 5$ to 18, at a pressure of 5 mm.

Fig. 3.—Showing the absorption of the principal series lines from $m = 7$ to 42, at a pressure of 46 mm.

OBITUARY NOTICES

OF

FELLOWS DECEASED.

CONTENTS.

G. Lippmann

GABRIEL LIPPMANN, 1845–1921.

GABRIEL LIPPMANN was born near Luxemburg, his father being a native of Lorraine and his mother an Alsatian. He received his early education at home, and when his parents settled in Paris, entered the " Lycée Napoléon " at the age of thirteen. Ten years later he was admitted to the Ecole Normale.

Lippmann's pronounced individuality, which appeared so strongly, both in the subjects he selected for research and in his method of attacking problems, showed itself at an early age; but the boy, absorbed in his own thoughts and irresponsive to outside influence, was not marked out for a successful school career. Concentrating on what interested him, neglecting what did not appeal to his taste, he acquired an invaluable fund of useful but unremunerative knowledge, with the result that he failed in the examination of " agrégation," which would have qualified him for Government service as a teacher in one of the higher schools. His exceptional abilities could not, however, fail to impress the more discriminative of his masters, and while still *in statu pupillari* Bertin induced him to collaborate in the publication of the " Annales de Chimie et de Physique " by abstracting German papers. It was in this way that he first became acquainted with contemporary researches on electricity, a subject which was not then taught at the Sorbonne. He is reported to have drawn Ruhmkorff's attention to the desirability of synchronizing the periods of the primary and secondary windings of an induction coil, but the " business man," as frequently happens, was not amenable to the advice of an academic novice.

After his failure in the examination, those who knew Lippmann and were able to appreciate his great abilities had, fortunately, sufficient influence with the Government to secure for him the appointment to a scientific mission, which gave him the opportunity of visiting German institutions and studying the provisions there made for the teaching of science.

At Heidelberg, the Professor of Physiology, Kühne, showed him a well-known experiment, in which a drop of mercury, covered by dilute sulphuric acid, is seen to contract on being touched with an iron wire, and to regain its original shape when the wire is removed. Lippmann recognised that the effect must be due to a connection between electric polarization and surface tension. He obtained permission to conduct, in Kirchhoff's laboratory, a systematic investigation of the subject, and was thus led to the construction of the capillary electrometer, an instrument now in daily use.

In 1883, Lippmann was appointed Professor of Mathematical Physics in the Faculty of Science at Paris. Three years later he succeeded Jamin as Professor of Experimental Physics, and became Director of the Research Laboratory which was subsequently transferred to the Sorbonne. He retained this position until his death.

Apart from his work on electro-capillarity, Lippmann obtained his most notable success in connection with colour photography. In a communication

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published in the "Revue des Sciences pures et appliquées," to which the writer of this notice is much indebted, M. A. Leduc states that as early as 1886 he explained in his lectures the general theory of the process by which the reproduction of colours by photography could be obtained. In the light reflected by a mirror the incident and reflected rays form together what in acoustics are called stationary vibrations, the planes of equal intensity being parallel to the mirror, and the distances between the maxima and minima proportional to the wave-length. If the mirror be covered by a sensitized film, layers are consequently formed in which the amount of deposited silver alters periodically. The principle when once stated is simple, but the practical execution presented difficulties that demanded all the patience and skill of an accomplished experimenter.

In a short communication to the "Académie des Sciences" in Paris, in 1891, Lippmann pointed out the two conditions which were essential to the successful application of the method. In the first place, the deposit of silver must be continuous or, at least, any granules formed must be small compared with the wave-length of light. The second condition demands an optical contact between the film and a good reflecting surface, which can best be secured by using mercury as the reflector. In practice, the glass plate carrying the film is attached to a hollow dish that can be filled with the liquid metal. After exposure, the mercury can be removed and the plate developed in the ordinary way.

The photographs obtained in this manner were at first defective, owing to the varying sensibility of the photographic film for different parts of the spectrum. Lippmann could report some improvement in the following year, and in 1893 he presented to the Académie des Sciences photographs taken by MM. Auguste and Louis Lumière, in which the colours were reproduced with perfect ortho-chromatism. An interesting variation of the process is described in another communication ('C. R.,' vol. 115), where it is shown that films impregnated with bichromate of potash are modified by the action of light which renders it less hygroscopic. The subsequent absorption of moisture affects the refractive index and an optically periodic layer is thus obtained. The complete theory of the reproduction of compound colours was published by Lippmann in 1894, but its essential points are contained in a paper by Lord Rayleigh, published in the 'Philosophical Magazine' in 1887, in which the author suggested that laminated structures produced by stationary luminous waves might explain the reproduction of coloured spectra such as were obtained by Edmond Becquerel as early as 1848.

Lippmann's scientific output, measured in pages of print, was not extensive; his communications to the Académie des Sciences were short, but invariably contained some original idea and illuminated the essence of his subject. As a member of the Board of the Bureau des Longitudes his attention was drawn to the exact measurement of time, and his contributions towards the perfection of experimental methods were always of interest and sometimes of considerable value. He realised at an early date the great assistance of

photographic registration, and an ingenious method of eliminating the personal equation in measurements of time was published in 1895. He dealt with the question of getting rid of the irregularities of pendulum clocks ('C. R.,' vol. 122, 1896), and his device for comparing the times of oscillation of two pendulums of nearly equal period ('C. R.,' vol. 124, 1897), deserves greater attention than it has received. His most important contribution to Astronomy was the invention of the cœlostat. In the so-called siderostats, which are in general use, the image of a star can be made to remain stationary while the star itself pursues its diurnal motion, but at the same time the images of surrounding stars partake of a rotational motion round the central point. This is entirely avoided in the cœlostat, so that an area in the sky of finite extension can be reduced to rest for a sufficient time to allow a lengthened photographic exposure.

Like most men of original mind, Lippmann was much absorbed in his own thoughts, and sometimes went over ground that had already been covered by others; occasionally one finds cause for regret that he appeared to lose interest in a subject when he had surmounted its difficulties, but before his work could be readily utilised by others. It is nevertheless of interest that in 1905 he independently enunciated the principle of the isostacy of the earth's crust ('C. R.,' vol. 136, p. 1172), and that two years later he described, under the title of 'Thermoendosmose des gaz,' an interesting phenomenon first discovered by Osborne Reynolds.

Attention may also be drawn to a few of his many ingenious devices which may prove useful, though some of them require further elaboration in detail. In 1901 Lippmann described a new form of galvanometer, which could be made absolutely astatic ('C. R.,' vol, 132, p. 1161). In 1902 he showed how small changes in the level of a mercury surface could be observed to a higher degree of accuracy than by the methods in common use ('C. R.,' vol. 135, p. 831); in 1910 he obtained a perfect electric connection that did not require the application of any pressure at the point of contact ('C. R.,' vol. 158, p. 1015). A new form of seismograph giving directly the acceleration of the earth's movement (described in 1909) is not only of theoretical interest, but may have a great future in its practical application ('C. R.,' vol. 148, p. 138). Its main principle consists in giving to a source of light a movement depending on the velocity and acceleration of the earth's motion and observing the image through a lens attached to the weight of a pendulum. Lippmann showed how the adjustments can be made so as to register the correct acceleration, but does not indicate how far he had tested the method.

Lippmann was elected a Foreign Member of the Royal Society in 1908, and was awarded the Nobel Prize in 1908. He died on July 31st, 1921, on board ship, during his return from a journey to Canada and the United States, in which he took part as a member of the mission sent out by France under the leadership of Maréchal Fayolle.

A. S.

THOMAS PURDIE, 1843–1916.

SOME centuries hence, when the present time and the Great War with which it has been overwhelmed can be seen in their true perspective, interest may be aroused as to how this country was almost suddenly able to produce enormous amounts of divers chemical materials, in the previous manufacture of which it had little or no experience. It will then perhaps be understood, as it is certainly but little realised now, that this memorable achievement was only rendered possible through the circumstance that at our universities and other academic institutions there had been for a generation before a small body of men, who, subsisting on very inadequate salaries and without any prospect of other worldly recognition, had been devoting themselves in their leisure (for it was not generally regarded as part of their academic duties) to the pursuit of pure chemical research. These men had associated with themselves in their scientific labours a select few of their more promising pupils, to whom they had succeeded in imparting some of their love and enthusiasm for the search after new knowledge for its own sake, and without any idea of recompense as understood by the exoteric public. This devoted band of men had during the generation preceding the war been successful in building up a British School of Chemical Research, which, although limited as regards the number of workers, was perhaps second to none in respect of the quality of its output. It was this school of chemical research, already in being, that rendered possible the supply of advice and of *personnel* necessary for the manufacture of the varied chemical products, without which this terrible war could never have been carried on with any possibility of success by a country the rulers of which, in their complete and unashamed ignorance of science, had taken no adequate steps to provide for.

Amongst the builders of the British School of Chemical Research there was certainly none more ardent or disinterested than Thomas Purdie, who for some twenty-five years occupied the Chair of Chemistry in the University of St. Andrews. The success of his labours is attested by the fact that, amongst the chemists who came to the assistance of the country in the hour of need, some of the most prominent were men who had received their initiation into research as his pupils.

Purdie was born at Biggar, Lanarkshire, on January 27, 1843, his father, whom he lost in early childhood, being a banker in that town. His upbringing devolved mainly on his mother, to whom he was deeply attached, but he was also much indebted in a variety of ways to a childless paternal uncle, a successful Edinburgh business man, whose resources were often placed at the disposal of the nephew, in whose development he took a very real interest.

Purdie received his school education at the Edinburgh Academy, where his literary and classical tastes appear to have been aroused by the
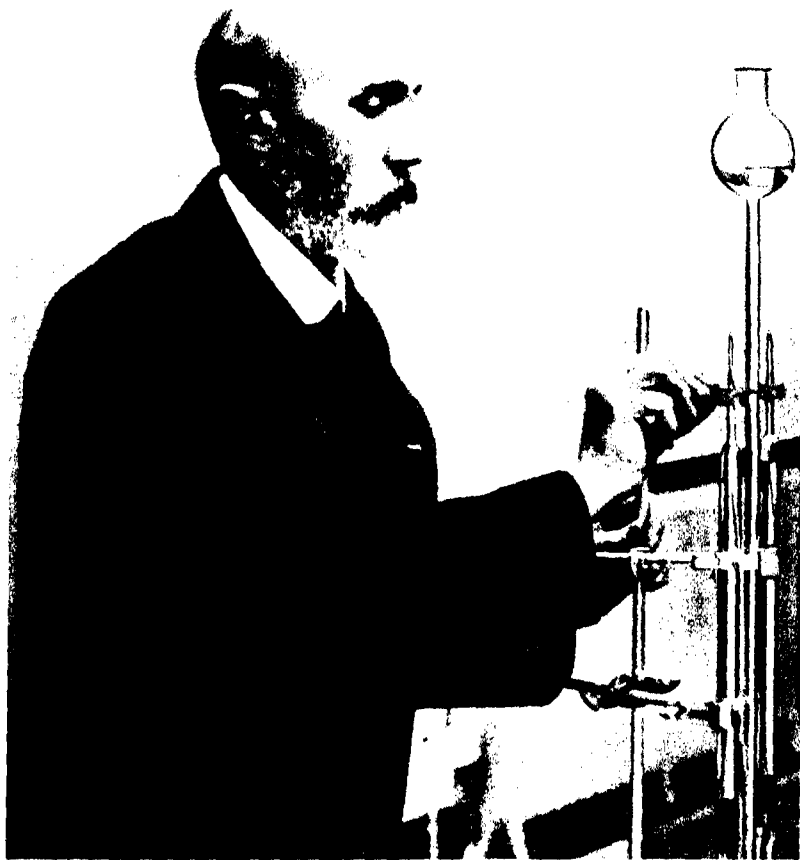
Thomas Purdie

stimulating personality of D'Arcy Thompson, the accomplished Greek scholar and father of the well known zoologist, hellenist, and biological philosopher, the present occupant of the Chair of Natural History at St. Andrews. On leaving school, Purdie, who was intended for a business career, was sent to Spain, where he acquired a sound knowledge of the language, and incidentally became attracted to mineralogy, and this doubtless influenced his choice of a profession later on. After a short experience of commercial life, however, he changed his intentions, and in the early sixties of the last century he embarked with a cousin for South America to take up farming in the Argentine. A large plot of land was purchased by the young pioneers, who established an *estancia*, which, owing to the unsettled state of the country, was the scene of many thrilling adventures, of which Purdie had interesting stories to relate. To those who later only knew him in the laboratory and in the lecture-room, it was difficult to picture this eminently peaceful man carrying on a defensive warfare against the marauding bands of Indians which periodically attacked the farm, and ultimately led to his abandoning the enterprise, in consequence of the financial embarrassment to which these frequent and unwelcome visitations gave rise.

The seven years which Purdie spent in South America, although terminating in failure from the common-place point of view, must have actually been of great value to him in developing his character and in broadening his outlook on life, by bringing him in contact with people, aspects of nature, and social conditions so profoundly different from those to be met with at home. This chapter in his life no doubt served as a permanent corrective to those Philistine influences which were the bane of those exclusively reared in Great Britain during the Victorian era, and it was the freedom from those confining prejudices and conceits which conferred on Purdie much of the charm of his engaging personality. These years had also stirred his scientific interests, for no actively intelligent man can pursue agriculture without being drawn into that logical study of natural phenomena which we call Science, whilst in Purdie's case the flora of the pampas and the geology of the Andes had attracted his special attention.

It was on his return to England that Purdie, now about 29 years of age, had the courage to start on an entirely new career. He used to ascribe his choice to a chance conversation with Huxley, whom he happened to meet under the cliffs at St. Andrews, with which Purdie was already at that time associated through his uncle being the owner of "Castlecliff," the principal residence there. Purdie having made up his mind, put his foot on the bottom rung of the ladder which he was aspiring to scale, and entered as a student at the Royal School of Mines. Here he came under the influence of the teachers by whom that Institution was then adorned—Huxley, Edward Frankland, Guthrie, Percy, and Warington Smyth. That he was a student of distinction is shown by the fact that, on his obtaining the Associateship, he

was, in 1875, appointed by Frankland as one of the Demonstrators in the Chemical Laboratories at South Kensington. It was when acting in this capacity that the present writer, then a second-year student of chemistry, made Purdie's acquaintance.

After spending some four years as a Demonstrator at South Kensington, Purdie decided to widen his chemical and academic horizon by proceeding to Germany, where, in the University of Würzburg, he entered the laboratory of Johannes Wislicenus, to whom at that time Frankland was forwarding those of his pupils who aspired to the acquisition of those finishing touches in chemical training which the atmosphere of a German university was alone capable of imparting.

Purdie went to Würzburg in the winter term of 1878, and a few months later married Miss Marianne Rotherham, of Coventry, who during the remaining thirty-six years of his life was his devoted and constant companion in sickness and in health, and whose personal charm was so largely instrumental in securing the success of his later social activities as an academic teacher at St. Andrews.

Purdie's research work for the degree of Ph.D. was continued at Würzburg until 1880, and during this period of two years the hospitality dispensed at the *ménage* of their married colleague was greatly appreciated by a number of British, American and German students. Amongst these were W. H. Perkin, junr., A. G. Perkin, Dobbin, Leonard Thorne, Burton, Gutzeit, Bischoff, and the writer. The great personal magnetism of Wislicenus exercised a deep and lasting influence on Purdie, not only in stimulating that enthusiasm for research which was so conspicuous to the end of his life, but in revealing to him, as it did to others, how a great department can be successfully directed, granted the possession of a certain personal equipment by the chief, without having recourse to any autocratic prerogative or actual manifestation of authority. Purdie's subsequent career at St. Andrews showed that he possessed in a high degree this personal equipment—unfailing and sympathetic goodwill towards assistants and students, unswerving adherence to justice in all his dealings, together with a quiet dignity as unassailable as it was unprovocative.

Soon after his return to England, Purdie succeeded Dr. Frank Clowes as Science Master at the Grammar School, Newcastle-under-Lyme, in 1881, and it was not until 1884, at the ripe age of 41, that he obtained wider scope for his energies and ability by his appointment to the Chemistry Chair at St. Andrews in succession to Prof. Heddle.

From the very outset it was Purdie's ambition to develop a Chemical Department in which original investigation, carried out both by the Professor and by his assistants and senior students, would form an integral and prominent feature. With the optimism of the idealist, he saw no reason why a Chemistry School such as he had seen in full operation in the small university towns of Germany should not be realisable at St. Andrews. He determined, in fact, to establish at the smallest Scottish university

something which did not exist at the time at the larger and more renowned Universities of Edinburgh, Glasgow and Aberdeen. To achieve this goal Purdie devoted all his energies, both physical and mental, as well as his private resources, nor did he allow himself to be discouraged by numerous disappointments or by the prostration which attended the more and more frequently recurring attacks of asthma, by which distressing malady the later years of his life were overshadowed. His will to succeed where others had failed was so indomitable that he was able to overcome obstacles which would have induced less resolute men to abandon the struggle.

Like a number of Wislicenus' pupils, Purdie was attracted by the problems of stereochemistry, and more especially those relating to optical activity and the asymmetric carbon atom, in the investigation of which Wislicenus had been one of the earliest pioneers. It was in this field that Purdie and his coadjutors laboured so incessantly and with ever-increasing success.

The progress of Purdie's scheme for establishing a School of Chemical Research at St. Andrews can be followed by a survey of his publications in the 'Transactions of the Chemical Society.' From 1885-87 he appears as a solitary worker, making contributions in his own name only, but from 1888 onwards to 1910 we find his name invariably associated either with those of his assistants or senior students, thus showing that the exotic plant which he had brought with him from Würzburg-on-the-Main had taken root and become acclimatised on the barren shore of St. Andrews Bay. Practically, all these joint contributions have reference to optically active carbon compounds. In this place it will only be necessary to call special attention to two groups of these publications.

It is well known to stereochemists that Pasteur, in his classical researches on optical activity, had at the very outset the good fortune to happen upon the comparatively rare phenomenon of an inactive racemate crystallising not as such but as a mixture in equal quantities of the optically active antipodes. In his first entry into the field of optical activity Pasteur found, in fact, that the optically inactive solution of sodium ammonium racemate yielded crystals which were not homogeneous, but consisted of a mixture in equal quantities of sodium ammonium *dextro*-tartrate and sodium ammonium *lævo*-tartrate respectively, and but for his apparently by chance lighting on this comparatively exceptional phenomenon it seems probable that his subsequent progress in unravelling the fundamental mysteries of optical activity would have been greatly delayed. By availing himself of this discovery Pasteur devised a method for easily obtaining from optically inactive racemic acid the *dextro*-tartaric and *lævo*-tartaric acids of which it is made up; for by preparing a supersaturated solution of sodium ammonium racemate, and introducing a crystal of sodium ammonium *dextro*-tartrate, a crop of crystals of the latter compound is obtained, whilst by introducing a crystal of sodium ammonium *lævo*-tartrate into a similar solution of the racemate a crop of sodium ammonium *lævo*-tartrate crystals makes its appearance. Purdie had the luck to meet with precisely the same phenomenon in the case of the zinc ammonium

salt of inactive lactic acid, and was thus able to effect a simple, speedy, and highly elegant "resolution" of inactive lactic acid into the optically active enantiomorphs or antipodes, *dextro-* and *lævo*-lactic acids, of which it is composed. In this manner these very important active compounds can be readily obtained in large quantity.

The vast edifice of organic chemistry, which, unfortunately, is practically a sealed book to all but those who have pursued a laborious course of study in this branch of science, whilst its fruits have become indispensable to the everyday life of the civilised world, has been reared by the discovery of chemical reactions which, by the possibility of their wide application, enable the most varied arrangements of the atoms in carbon compounds to be brought about. The discovery of such a reaction stands to the credit of Purdie and his pupils, and as is so frequently the case, the discovery was made accidentally in the course of investigations having a totally different objective. Purdie was engaged in the preparation by a well-known method of the esters of certain optically active hydroxy-acids by acting with alkyl iodides on the silver salt of the hydroxy-acid (*e.g.*, lactic or malic acid), with the result that he found that the alkyl lactate or alkyl malate so formed had a considerably higher rotation than when the same compounds were prepared by other methods. This at first he supposed to be due to the compounds of higher rotation being of greater purity than the ones of lower rotation; but before long he discovered that precisely the opposite of this was the truth, and that the products of higher rotation were contaminated in each case by a compound (of high rotation) which had been simultaneously formed by another and hitherto unsuspected reaction between the ingredients used in his experiments. Thus by acting with ethyl iodide on silver lactate he had obtained not only ethyl lactate, but also some ethyl ethoxypropionate, which, having a much higher rotation than ethyl lactate, caused the mixture also to have a higher rotation than that of pure ethyl lactate. Similarly, from ethyl iodide and silver malate he had obtained a mixture of ethyl malate and ethyl ethoxysuccinate, giving a higher rotation than pure ethyl malate. By the further study of this subsidiary reaction, taking place in the above cases, Purdie elaborated a highly important method for the alkylation of hydroxy-compounds in general. This, which in future will doubtless conveniently be designated as the "Purdie reaction," consists in treating the hydroxy-compound, either in the homogeneous state or dissolved in a neutral solvent, with dry silver oxide and alkyliodide, when alkylation of the hydroxy-group is readily effected.

This reaction was at once exploited by Purdie and his pupils in the systematic investigation of those numerous and important hydroxy-compounds which constitute the sugar-group (aldoses, ketoses, polysaccharides, glucosides, etc.). These researches, begun in conjunction with J. C. Irvine and other pupils (R. C. Bridgett, D. M. Paul, R. E. Rose, and C. R. Young), were continued after Purdie's retirement, in 1909, by Irvine, his successor in the Chair, and by him they have been zealously prosecuted up to the present time

with such conspicuous success that they bid fair to form a worthy comple-ment to the earlier monumental work of Emil Fischer.

In speaking of Purdie's pupils mention must also be made of work carried out by some after leaving St. Andrews. Thus, more especially should reference be made to the well-known researches of Prof. Alexander McKenzie, culminating in his discovery of "the asymmetric synthesis," the goal so eagerly striven for by many stereochemists, including Emil Fischer himself.

Further evidence of the vitality of the Chemical School founded by Purdie is afforded by the fact that during the War the St. Andrews Laboratory was one of the most active centres in which those innumerable chemical problems to which the circumstances of that great conflict gave rise were wrestled with and for the most part successfully solved.

Thus before the end of his life Purdie had the satisfaction of seeing the Chemical Department, which his creative energy and resource had raised from the dust and ashes of bankrupt mediævalism, obtaining wide recognition as a focus of fruitful research and performing work of the utmost practical importance to the nation in the hour of its sorest need.

It was not, however, Purdie's intention that the prosperity of this Chemical Department at St. Andrews should terminate with his own life, a precarious one at best, but that it should be, as far as he could ensure it, a permanent establishment capable of holding its own after he had passed away. So loyally was this wish of his carried out by his wife, who survived him only two years, that the residue of her estate, amounting to about £25,000, was, by her will, bequeathed to the University, to be applied exclusively to the promotion of research in chemistry at St. Andrews. This sum, with that made over during Purdie's lifetime, gave a total endowment in 1919 of approximately £33,000 for the prosecution of chemical investigation in the department of which he laid the foundations on his taking up the Chair in 1884. It would surely be difficult to point to any more illustrious example of whole-hearted and enduring devotion to science than is furnished by this record.

We are generally accustomed to associate conspicuous achievements, such as have been described above, with persons of great and manifest vigour, a forceful individuality, endowed with exuberant health and spirits, or with other external signs of available energy; but in Purdie there was none of this. The central fire was wholly concealed by the tall, frail, and somewhat languid figure and placid features, as well as by the modest, retiring, and self-effacing deportment, whilst the melancholy and sympathetic eyes alone would, as occasion demanded, glow with enthusiasm, or twinkle with a sense of humour, mirroring forth the rare soul which dwelt within.

No account of Purdie's work at St. Andrews would be complete without some reference to the social activities which centred around 14, South Street, the charming but modest home in which he and his ideal helpmate dispensed a genuine but unostentatious hospitality to a wide circle of friends, colleagues and students. It was, in the truest sense of the words, an "open house,"

sought for purposes of friendly intercourse, for intellectual discussion, for counsel, and for sympathy in joy or sorrow.

Purdie took his relaxation in golf on the far-famed links, in foreign travel, and in trout-fishing in various remote parts of Scotland, latterly at Finsbay, on the Island of Harris, where both he and Mrs. Purdie will long be remembered for their kindly relations with the crofters.

Purdie's scientific work was recognised by his election to the Fellowship of the Royal Society in 1895, by the LL.D. degree of Aberdeen University, which was conferred on him in 1894, whilst the very special services which he had rendered to St. Andrews were acknowledged by the conferring of the LL.D. degree of that University, and the title of Professor Emeritus on the occasion of his retirement from the active duties of his Chair in 1909.

Purdie succumbed to heart failure on December 14, 1916, at the age of 73, and was buried in the Cathedral Cemetery of the grey little city which he loved so well, and in which he laboured so long.

<div align="right">P. F. F.</div>

GEORGE BALLARD MATHEWS, 1861–1922.

GEORGE BALLARD MATHEWS was born in London on February 23, 1861. His father, George Mathews, was the son of a Herefordshire yeoman farmer, and engaged for many years with a London business house. His mother's maiden name was Harriet Ballard, daughter of George Ballard, secretary to the Board of Inland Revenue, and a remarkable man from whom Mathews inherited much of his personality and intellect. From his mother he inherited his literary and musical abilities, his interest in general subjects, and his powers of calculation.

The family returned to Herefordshire in 1866, and Mathews, in 1872, entered Ludlow Grammar School, where his brilliant intellect soon asserted itself. Records of 1875 state that he was first in the top form with prizes in Mathematics, French, Drawing, Form Prize, and Parents' Prize. During the four years, 1874–78, he was captain of the school. From the Rev. W. C. Sparrow, one of the most successful Headmasters of the school, he received instruction in Hebrew as well as in Greek and Latin.

There followed a year at University College, London, of which body he afterwards became a Fellow, during which he attended Henrici's lectures on geometry, and began to study Sanscrit. In 1879 St. John's College, Cambridge, offered him the senior scholarship of his year in either Mathematics or Classics. Carrying out his intention of reading for the Mathematical Tripos,

he became a private pupil of Mr. W. H. Besant of St. John's. The keen competition for leading places in the Tripos of this period had brought fame to Mr. E. J. Routh as a coach. All the abler candidates went to Routh as a matter of course, for Routh had a long series of senior wranglers to his credit. However, Mathews' name was read out first in the list of 1883, this being the only break in a succession of about thirty consecutive seniors trained by Routh.

In 1884, Mathews was appointed to the Chair of Mathematics in the newly-constituted University College of North Wales at Bangor, and in the same year was awarded a Smith's Prize and a Fellowship at St. John's. His colleagues at Bangor were all of the same generation as himself, and included such men as Profs. Andrew Gray, James Dobbie, and the late Henry Jones, under the leadership of Principal Harry R. Reichel (the last three named have all since been knighted). Writing in ' Nature ' (June 3, 1922), of the period which followed, Prof. Gray says : "[Mathews] came full of eager enthusiasm for the teaching of mathematics and for original mathematical work, and for ten years laboured hard in the hope of founding something like a school of mathematical study in North Wales. But, alas ! these hopes were dashed. Perhaps he was a little impatient, and I certainly did my best to counsel him to wait, and to find out the effect of the new Welsh University on the studies of the place, but without effect. The best of the Welsh students were at that time attracted by the Neo-Hegelian philosophy, and some of them, as seems to be the way with such students, seemed not a little proud that their mental tendencies were not mathematical. To this curious type of intellectual pride Mathews referred eloquently in the posthumous paper published in ' Nature ' of April 22. In that paper, he lamented the revival of the fallacious arguments for the supremacy of the Latin-Greek classics as an educational instrument; but he in no way under-valued classical culture, only he thought that, to an Englishman, the inheritor of a copious and flexible language, and of a literature unparalleled in the past, a training in Latin and Greek was far from indispensable and might have its disadvantages."

The Bangor Chair was resigned in 1896, and shortly followed (1897) by Mathews' election into the Royal Society, on the Council of which he served for a year. He also served on the Council of the London Mathematical Society from 1897 to 1904. Having returned to Cambridge he was appointed University Lecturer in Mathematics, and acted for a year (1904–5) as Mathematical Secretary to the Philosophical Society. The Cambridge appointment, like the earlier one in Bangor, was resigned on account of temperament, and he returned to live in Bangor. Since 1911 he held a special lectureship in the North Wales College, and again acted as Professor there during the two sessions 1917–19. The honorary degree of LL.D. was conferred by Glasgow University in 1915.

While thoroughly familiar with all branches of pure mathematics, Mathews' main interests were in the theory of numbers and projective geometry. The

theory of numbers, which, in its widest sense, is the theory of discrete, as opposed to continuous, magnitude, has passed through four well-defined stages of development. First there came the period of Diophantine Analysis proper, of which the greatest exponents, after Diophantos among the ancient Greeks, were Fermat and Euler. In this, the general problem is to determine all the solutions in rational numbers of a system of $m (< n)$ algebraic equations

$$R_i (x_1, x_2, \ldots x_n) = 0, \ i = 1, 2, \ldots m.$$

Next came the discovery of the law of quadratic reciprocity which rendered possible a discussion of quadratic arithmetical forms, so ably expounded by Gauss in the "Disquisitiones Arithmeticæ." Such writers as Lejeune-Dirichlet, Eisenstein, and Stephen Smith added much to what Gauss had done, and a scholarly introduction to the whole theory was given by Mathews in his "Theory of Numbers" of 1892. A problem which arises in the theory of quadratic forms (the determination of the class-number) was the forerunner of the analytical theory which is intimately bound up with certain transcendental functions of a complex variable. This theory, which has recently received much attention from Prof. E. Landau, Prof. G. H. Hardy, and the late S. Ramanujan, had little atraction for Mathews, though his book contains an introduction to it.

The fourth stage was marked by Dedekind's discovery of his theory of ideal numbers, which completely restore to a system of algebraic numbers certain factorisation properties of ordinary integers that appear at first to be lost. Mathews' was probably the first mind in England to realise the far-reaching effect of Dedekind's discovery, two papers by him on the subject appearing in the London Mathematical Society's Proceedings of 1892.

The tract "Algebraic Equations" on a kindred topic, written fifteen years later, contains a masterly exposition of Galois' theory, completed by Jordan and others, showing how the different types of irrationality which can be defined by an algebraic equation are associated with different types of group.

Written in collaboration with Prof. Andrew Gray and mainly concerned with physical applications, the "Treatise on Bessel Functions" (1894) is still a standard work. The "Projective Geometry" (1914), inspired by Henrici's lectures in London many years before, contains two unusual features: first, an exposition of the logical groundwork of the subject; and, secondly, an account of Staudt's theory of complex elements (whereby a real involution defines a complex point or line). Mathews also brought out a new edition (1904) of R. F. Scott's "Determinants," and contributed articles on " Number " and " Universal Algebra " to the 1910 edition of the "Encyclopædia Britannica."

Most of Mathews' technical papers appeared in the London Mathematical Society's Proceedings, or in the "Messenger of Mathematics." Some of the earliest, beginning in 1886, are connected with Fermat's Last Theorem, a question which absorbed much of his attention at intervals during the rest

of his life. Being firmly convinced of the veracity of Fermat's statement, he tried to approach the problem by such methods as might have been devised in Fermat's day. His last contribution to the subject appeared in a review published in 'Nature' of January 5, 1922. .

A few of the earlier papers deal with geometrical subjects, such as twisted quartic curves, geometry on a quadric surface, and porisms. Nearly all the rest have an arithmetical bearing. Several papers discuss points connected with the Gaussian theory of quadratic forms, the subject of his book. In 1892 he wrote on quadratic forms with complex coefficients, a subject to which he returned twenty years later. In early days he corresponded freely with Cayley and Sylvester.

Among the specialised branches of the higher arithmetic Mathews was mainly interested in the complex multiplication of elliptic functions. Being an assiduous disciple of Dedekind and Klein, he fully realised the fundamental character of the absolute invariant $j(\omega)$ and of the type of irrationality involved in it. Papers written in the nineties, when Sir George Greenhill and Mr. Russell were working at the subject too, give special detailed properties of the lemniscate functions. He also showed the significance of Klein's principal moduli and calculated some new class-invariants. Returning to the subject in later years, he produced a fuller manuscript on the lemniscate functions: its publication has been delayed by the war and his subsequent illness.

Ever since the mid-eighties Mathews was a frequent contributor to 'Nature' on mathematical topics. His articles and reviews, most of which appeared over the initials " G. B. M," were always written in a careful and scholarly style; they contained his considered opinion on the book or point concerned. His keen yet kindly criticism was undoubtedly of the greatest service to the many writers whose work passed through his hands. In conversation with the present writer he once expressed the opinion that some of his best work had appeared in 'Nature' reviews.

A man of simple tastes and naturally retiring by disposition, Mathews expressed sound judgment on both men and affairs. Some of his views were those of an idealist and hardly feasible in the domain of practical politics. His capacity for maturely grasping everything with which his mind came into contact made him unique in the experience of his friends. Only one or two sides of so versatile a man's brilliant intellect really appealed to most people. When he was appointed Professor of Mathematics at Bangor, at the age of twenty-three, it was manifest that he could equally well fill four or more chairs in the College. Again, to quote Prof. Gray: " Mathews had a knowledge of Latin and Greek as minute and accurate as that generally possessed by professional classical scholars. He wrote pure and elegant Latin. I remember his amusing himself by turning into Latin prose an original philosophical dissertation which had happened to come into his hands and had arrested his attention. I remember also some Latin verses which he published anonymously, and which were much praised by a very

eminent scholar. He wrote also charming English essays in the style of Charles Lamb, of whom he was a great admirer. These, I fear, are lost, but one of them, 'On a Cock-loft,' was a perfect gem, a charming piece of the most natural and simple prose."

A humorous controversy in Latin Elegiacs between Profs. Arnold and Mathews, in which Mathews did not come off second best, inspired Principal Reichel's epigram, addressed, in the College Magazine, to a mathematical student who had been reading Mathews' verses :—

> Versibus an numeris noster praestantior anceps
>   Mattius ; attonito cur puer ore siles ?
> Qui numeros dicit vult idem dicere versus,
>   Testibus innumeris, o numerose puer.

In the early days at Bangor Mathews began to learn Arabic, and spent much time of later years in reading and translating Arabic poetry. His translations are full of the spirit of the original lines; it is to be hoped that some of them will be published later.

Mathews' knowledge of music, again, was fully as advanced as that of most professional musicians. His copies of Gauss and Bach were placed together on the same shelf, and he considered some of Sir Edward Elgar's compositions to be as fine as the work of Beethoven and Handel.

Undoubtedly, the strength of his numerous interests prevented him from making the most of his mathematical work. His name will be mainly remembered in connection with the higher arithmetic.

The last three years of his life were clouded by a series of operations for cancer, which finally gained the mastery. He died, unmarried, in a Liverpool nursing home on March 19, 1922.

<div align="right">W. E. H. B.</div>

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